THE

PHYSICAL SOCIETY

OF

LONDON.

PROCEEDINGS.

VOLUME XXIX.—PART I.

DECEMBER 15, 1916.

Price to Non-Fellows, **4s.** *net, post free* **4/3**.

Annual Subscription, **20/-** *post free, payable in advance.*

Published Bi-Monthly from December to August.

LONDON:
"THE ELECTRICIAN" PRINTING & PUBLISHING CO., LTD.,
1, 2 AND 3, SALISBURY COURT, FLEET STREET

1916.

THE PHYSICAL SOCIETY OF LONDON.

1916-17.

OFFICERS AND COUNCIL.

President.

PROF. C. VERNON BOYS, F.R.S.

Vice-Presidents.

WHO HAVE FILLED THE OFFICE OF PRESIDENT.

PROF. G. C. FOSTER, D.Sc., LL.D., F.R.S.
PROF. R. B. CLIFTON, M.A., F.R.S.
PROF. A. W. REINOLD, C.B., M.A., F.R.S.
SIR W. DE W. ABNEY, R.E., K.C.B., D.C.L., F.R.S.
PRIN. SIR OLIVER J. LODGE, D.Sc., LL.D., F.R.S.
PROF. SILVANUS P. THOMPSON, D.Sc., F.R.S.
R. T. GLAZEBROOK, C.B., D.Sc., F.R.S.
PROF. J. PERRY, D.Sc., F.R.S.
C. CHREE, Sc.D., LL.D., F.R.S.
PROF. H. L. CALLENDAR, M.A., LL.D., F.R.S.
PROF. A. SCHUSTER, PH.D., Sc.D., F.R.S.
SIR J. J. THOMSON, O.M., D.Sc., F.R.S.

Vice-Presidents.

W. R. COOPER, M.A., B.Sc.
F. E. SMITH.
S. W. J. SMITH, M.A., D.Sc., F.R.S.
W. E. SUMPNER, D.Sc.

Secretaries.

PROF. W. ECCLES, D.Sc.,
Finsbury Technical College, Leonard Street, E.C.

R. S. WILLOWS, M.A., D.Sc.,
Cass Technical Institute, Jewry Street, Aldgate, E.C.

Foreign Secretary.

R. T. GLAZEBROOK, C.B., D.Sc., F.R.S.

Treasurer.

W. DUDDELL, F.R.S.
56, *Victoria Street, S.W.*

Librarian.

S. W. J. SMITH, M.A., D.Sc., F.R.S.
Imperial College of Science and Technology.

Other Members of Council.

H. S. ALLEN, M.A., D.Sc.
PROF. W. H. BRAGG, M.A., F.R.S.
S. D. CHALMERS, M.A.
PROF. G. W. O. HOWE, D.Sc.
PROF. J. W. NICHOLSON, M.A., D.Sc.
C. C. PATERSON.
C. E. S. PHILLIPS, F.R.S.E.
PROF. O. W. RICHARDSON, M.A., D.Sc., F.R.S.
G. F. C. SEARLE, Sc.D., F.R.S.
F. J. W. WHIPPLE, M.A.

I.—*The Application of the Kerr Effect to the Determination of the Saturation Values for Magnetism of Ferro-magnetic Metals, Compounds and Alloys.* *By* S. G. Barker, *D.I.C., Ph.D., King Edward VII. Research Scholar.*

Received September 4, 1916.

In the year 1876 Kerr[1] observed that the direction of vibration of plane polarised light was altered when the polarised ray was reflected from a ferro-magnetic mirror placed in a magnetic field. Further work on this phenomenon was done later by Gordon,[2] Fitzgerald,[3] Hall,[4] Kaz,[5] Righi,[6] Kundt,[7] Du Bois,[8] Sissingh,[9] Zeeman,[10] Ingersoll,[11] Foote,[12] Loria,[13] Martin,[14] and many others. It has been conclusively shown that the Kerr effect is only possible in the case of ferro-magnetic bodies such as iron, nickel, cobalt, iron oxides, &c., whilst diamagnetic bodies like bismuth have shown no appreciable effect. As well as the change of the plane of polarisation, yet another change is evident—namely, if the incident light is plane polarised, the reflected ray is elliptically polarised. The major axis of the ellipse corresponds to the new plane of vibration of the plane polarised light. In the simplest case of nearly vertical reflection either perpendicular or parallel to the plane of incidence of the polarised light, and with normal magnetisation, the rotation is dependent only on the wave-length and the strength of the magnetic field. This simple case is used exclusively throughout this work.

The dispersion curves throughout the spectrum have been investigated for the Kerr effect by a large number of observers, amongst whom Du Bois was one of the earliest, followed later

(1) J. Kerr, "Phil. Mag." (5), 3, p. 321, 1877; 5, p. 161, 1878.
(2) J. E. H. Gordon, "Phil. Mag." (5), 4, p. 104, 1877.
(3) G. F. Fitzgerald, "Proc." Roy. Soc., 25, p. 447, 1876.
(4) E. H. Hall, "Phil. Mag." (5), 12, p. 171, 1881.
(5) P. C. Kaz, "Diss. Amsterdam," 1871.
(6) A. Righi, "Ann. d. Chem. u. Phys." (6) 4, p. 443, 1885.
(7) A. Kundt, "Wied. Ann.," 23, p. 228, 1884; 27, p. 199, 1886.
(8) H. du Bois, "Wied. Ann.," 39, p. 228, 1890.
(9) R. Sissingh, "Arch. Neerland." (1), 27, p. 173, 1894.
(10) P. Zeeman, "Arch. Neerland.," 27, p. 252, 1894.
(11) L. P. Ingersoll, "Phil. Mag." (6), 11, p. 41, 1906; 18, p. 74, 1909.
(12) P. D. Foote, "Phys. Review" (2), 34, p. 96, 1912.
(13) St. Loria, "Ann. d. Phys.," 38, p. 889, 1912.
(14) P. Martin, "Ann. d. Phys.," 39, p. 625, 1913.

by Ingersoll, Loria, Martin and others. Ingersoll has confined his attention to the infra-red part of the spectrum and used wave-lengths between 1μ and 3μ. He accomplished this by means of a bolometer method. Du Bois investigated the curves for iron, nickel, cobalt and magnetite over the whole visible spectrum. In the present work the curves of Du Bois have been more accurately re-determined, and the number of points taken considerably amplified. These will be discussed later. Du Bois found that iron gave a negative rotation from the violet to the red with a probable minimum in the ultra-violet. Nickel gave a minimum in the yellow, and cobalt a minimum in the blue-green. Magnetite exhibited a positive maximum rotation in the yellow, and a zero value in the violet. Ingersoll prolonged these curves into the infra-red. He showed that for iron and cobalt there are well-defined negative maxima near $\lambda=1\mu$, and then quick decreases in numerical value. Nickel showed a more remarkable phenomenon in that between the wave-lengths $\lambda=1\mu$ and $\lambda=1{\cdot}5\mu$ the value passed through zero. Magnetite exhibited two inversion points. Du Bois has closely investigated the relation between the magnetic field strength and the Kerr rotation, and established the Kerr constant for various metals. Foote* examined the curves for ellipticity and dispersion. Loria and von Zakrzewski† attempted to find a relation between the Kerr effect and the optical constants of the metals. Chemists and metallurgists have placed us to-day in possession of many prepared ferro-magnetic substances. Hilpert‡ has produced metaferrites by combinations of different oxides with iron oxide. In all cases in this series he has maintained the identical structure of magnetite, FeO, Fe_2O_3, using the latter part as the acid radicle and simply substituting CuO, &c., for FeO. The iron parts of the compounds evidently carry the magnetic properties.

The object of the present work is to demonstrate the theory of du Bois§ that in the case of ferro-magnetic substances there exists a proportionality between the rotation (ε) and the intensity of magnetisation (I). When the maximum mag-

* P. D. Foote, "Phys. Review" (2), 34, p. 96, 1912.

† St. Loria and C. Zakzrewski, "Bull." de l'Académie des Sciences de Cracovie (A), 22, p. 275, 1910.

‡ S. Hilpert, "Ber. Deutsch. Chem. Ges.," 42, p. 2248, 1909.

§ H. du Bois, "Wied. Ann.," 31, p. 952, 1887; "Phil Mag.," 29, p. 301, 1890.

netisation is reached (I_m), the rotation (ε_m) will become constant. According to Du Bois, if the rotation be plotted as a function of the magnetising field—*i.e.*, $\varepsilon = F(H)$, then the value of I_m can be found. In the case of an infinite homogeneous plate, with normal magnetisation, the point of intersection of the straight line

$$\varepsilon = K.I. = K.H./4\pi$$

and the asymptote $\varepsilon =$ constant

gives an abscissa (x) whose value is $4\pi I_m$, where I_m is the saturation value. Loria began preliminary investigations of this point, but his results obtained with samples of quite irregular configuration were not at all concordant. In the present work specimens of iron, nickel and cobalt, and many other substances whose saturation values had been carefully determined, were taken as the groundwork on which to base the efficiency of the method. These specimens were all of the standard shape discussed later, and were investigated first of all. The values so obtained were in excellent agreement with those found by other methods. Later in the work various other materials of unknown saturation values were examined. The great advantage of this method is that the saturation value of a substance can be found when only a very small quantity is available. The mirrors used in all the tests were of the uniform size 2·5 mm. in radius and 0·5 mm. thick. The method of procedure and the description of the apparatus is set out below. The curves plotted show ε as $F(H)$, and the sign of the rotation is noted in every case. Loria found in his work that wave-length had an influence on the saturation value obtained. With the same material, using light of different wave-lengths, he obtained different saturation values from the different curves obtained. This work shows, as would be expected, that he was wrong, and that wave-length has no influence on the values obtained. His error was probably due to the irregular shape of his mirrors and the very few and insufficient number of points taken.

Description of Apparatus Used.

The apparatus used is illustrated in the accompanying diagram. The light from an arc lamp (in exceptional cases from the sun) was focussed on the slit of a Du Bois* mono-

* H. du Bois, "Zeitshr. f. Instrumenten.," 31, p. 1, 1911.

chromator, the slit of which was altered in width according to the intensity of illumination desired for any particular wavelength. In the extreme blue and red regions the slit was, with safety, made much wider, but in the green $\lambda=530{\cdot}0\mu\mu$ the width was uniformly kept at 0·15 mm. The light passed through the monochromator and emerged from the same through a slit of equal width to the one on which the light was incident. It was then immediately focussed on to a Du Bois half-shade polarimeter.* In this instrument the beam is reflected through an angle of 90 deg. by a mirror. It next passes through two Nicol's prisms and emerges as plane polarised light. The polarised beam passes onwards through a hole in the arm of a large Du Bois ring magnet, and emerges through the pole-piece by a vertical rectangular slit. From this it is incident on a small metallic mirror placed on the other pole-piece a small distance away. The return beam is received in the analyser, and the rotation is measured on the vertical scale by an optical arrangement as shown in the diagram. This system of taking readings enabled extremely small differences in the rotation to be measured with considerable accuracy. The light from an illuminated scale was reflected by a plane mirror on to another plane mirror attached to the analyser, and which rotated with it. From this it was reflected through a right-angled prism into a large magnifying telescope, by means of which the readings could easily be taken with great accuracy. The angle between the Nicol's prisms was 0·4 of a degree, and the mean error of reading about 0·01 of a minute. In certain exceptional cases the light was slightly elliptically polarised, but in no case to an extent sufficient to cause annoyance or error. The field was obtained by a large Du Bois ring magnet† of resistance 1·5 ohms. After applying strong currents it was found necessary to open the magnetic circuit and demagnetise the instrument by knocking. The intensity of the magnetic field was measured primarily by a ballistic method, and subsequently by means of a thin glass etalon with silvered back surface. The etalon was placed between the poles and the rotation of the plane of polarisation, when different fields were existing was measured as before. The etalon was always placed close to the metallic mirror—*i.e.*, the back pole. Owing to the reflection from the silvered back

* H. du Bois "Wied. Ann.," 46, p. 545, 1892.
† H. du Bois, "Wied. Ann.," 51, p. 549, 1894.

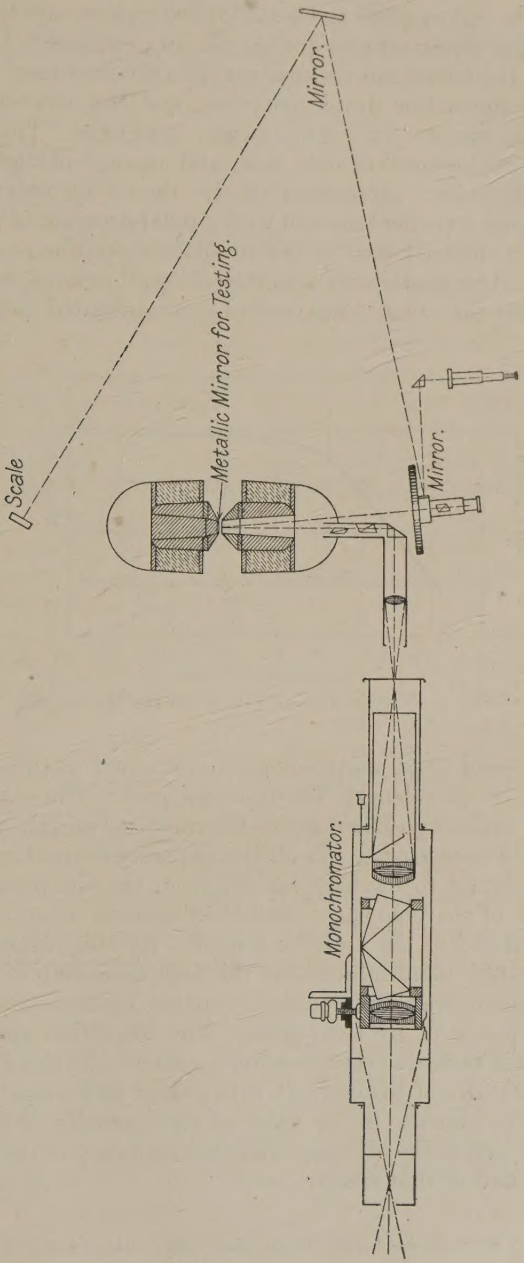


DIAGRAM OF APPARATUS.

surface, the light passed twice through the glass, and therefore the rotation observed was double the proper value. On commutating the current in the magnet coils the resultant rotation was four times the simple rotation, and for wave-length $\lambda = 530{\cdot}0\mu\mu$ was $4 \times 3{\cdot}26$ minutes per kilogauss. The etalon had a mean thickness of 0·35 mm. and an angle of slightly less than 20 minutes. According to the theory of polar armatures,* using a vertical slit and with a polar distance of 1·6 mm. the field in the back part of the air space should be practically uniform. This uniformity was tested for all mirrors used, and the results for cobalt and nickel are appended below. A

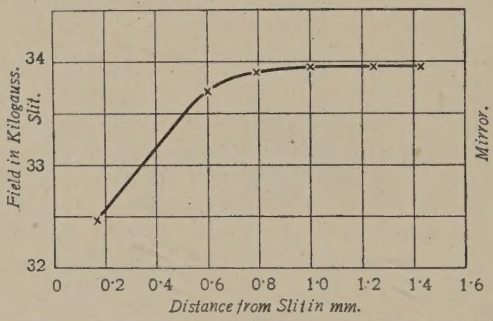


FIG. 1.—CONSTANCY OF FIELD COBALT MIRROR.

steady current of 20 amperes was maintained in the magnet, and light of wave-length $530{\cdot}0\mu\mu$ was used. The etalon was placed in various positions across the air space and the rotation determined in each case. In all the experiments performed the field was found to increase rapidly from the slit towards the mid-point of the pole space, and then became constant in the neighbourhood of the metallic mirror. By this means it was experimentally determined that the field immediately in front of the mirror was uniform and capable of measurement to within 1 per cent. by the etalon. The correction applied by Foote in his work was therefore unnecessary. Tables I. and II. give the results of experiment with cobalt and nickel mirrors to show the increase in the value of the intensity of the magnetic field across the air space and the constancy of the same in the back half of that space.

* H. du Bois, "Ann. d. Physik.," 42, p. 911, 1913.

TABLES I. AND II.

Distance of etalon from slit.	Cobalt mirror. Field in kilogauss.	Nickel mirror. Field in kilogauss.
0·17 mm.	32·48	30·65
0·60 mm.	33·71	31·88
0·80 mm.	33·89	32·30
1·05 mm.	33·94	32·48
1·25 mm.	33·94	32·48
1·43 mm.	33·94	32·48

All distances were measured to centre of etalon.

The mirrors for the measurement of the Kerr effect were mounted on cones of iron and inserted in a conical space in the pole-piece. The mirror itself consisted of a plane disc of circular dimensions, 2·5 mm. in radius and 0·5 mm. thick. This was the same in all cases. The mirrors were soldered on to the cones and then polished to give a plane and highly reflecting surface. In order to obtain uniformity of field (by Du Bois theory), the mirror was always placed at a distance of 1·6 mm.

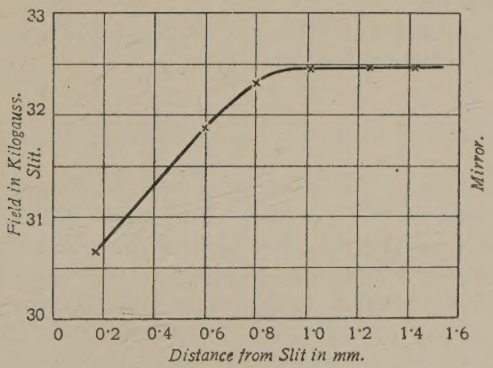


FIG. 2.—CONSTANCY OF FIELD NICKEL MIRROR.

from the slit. It was thought that the air in the space between the pole-pieces might be a possible source of error in enhancing the rotation, so a silver mirror was inserted between the poles. As the result of 100 independent readings of the rotation by commutating the current in the magnet coils, it was found that for the highest fields, using light $\lambda=506\ \mu\mu$, the rotation was 0·015′, and consequently within the limits of experimental error. After each set of readings for the saturation curve the etalon calibration was immediately taken and the field strengths calculated. There was no visible increase in the rotation due to the etalon for currents above 20 amperes.

Throughout the whole Paper the following notation will be used for the various quantities :—

H=Field intensity in kilogauss.
I_m=Saturation value in C.G.S.
ε_m=Maximum rotation.
K=Kerr's constant.
I=Magnetisation.
ε=Rotation in minutes of arc.
λ=Wave-length used in 10^{-6} mm.
s_m=Specific magnetisation.

The sign of the rotation is taken according to the usual convention that in the case of iron it is negative. Below are appended :—

1. The results of the determination of saturation values of materials which have been tested by other methods. This was done to justify the method.

2. Determinations of saturation values of ferro-magnetic metals and alloys.

3. Dispersion curves of these substances which have been more accurately determined than before.

Experiments with Metals of Known Values.

Electrolytic Iron.—(1) This material was kindly given to me by Dr. Gumlich, of the Physische Technische Reichsanstalt, Berlin, in 1914, and was a piece of iron the saturation value of which he had determined by the isthmus method. He gave the value as 1,705 C.G.S. units. The results are set out in Table III.

Table III.

Saturation curve. Iron (1). λ=530·0 $\mu\mu$.

Field in kilogauss.	Rotation in minutes.	Field in kilogauss.	Rotation in minutes
2·34	2·54	21·74	21·77
4·00	4·20	23·19	22·20
5·68	6·00	24·81	22·26
7·60	8·20	26·51	22·30
9·13	9·80	32·30	22·68
10·80	11·80	35·83	22·68
12·28	13·30	36·56	22·68
14·52	15·90	39·44	2·68
17·51	19·00	40·42	22·68
19·86	20·70	...	...

Rotation was negative throughout.

The results were plotted in Fig. 3, and it is easily seen that the value of x, the abscissa of the point of intersection of the asymptote and the saturation curve horizontal produced

$$x = 4\pi I_m = 21{\cdot}00 \text{ kilogauss.}$$

Therefore $I_m = 1{,}681$ C.G.S. units.

This agrees very well with the value given by Gumlich, the difference being 24, or 1·5 per cent.

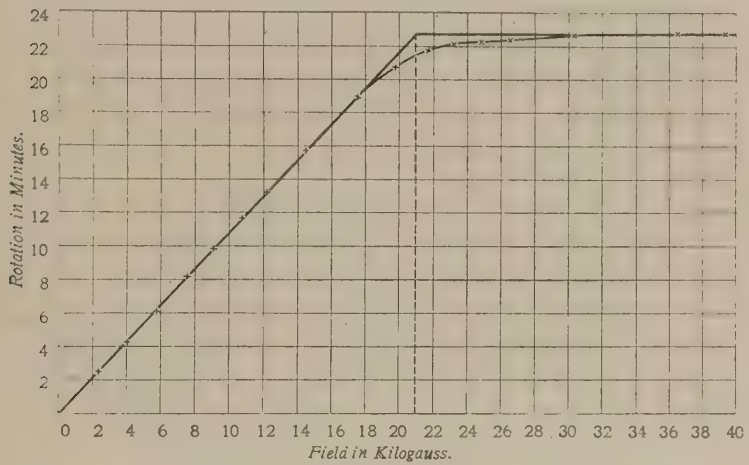


FIG. 3.—IRON (1). SATURATION CURVE.

Dispersion Curve.—The dispersion curve for the Kerr effect was also found for this specimen of iron. There is nothing unusual or extraordinary in it. The curve shows a rapid rise from the blue to the red end of the spectrum. The field used was 36·56 kilogauss, and it is evident from the curve, Fig. 3, that this is above the saturation value. The observations are in agreement with those of Martin and Foote.

Table IV. shows the figures obtained for the dispersion.

TABLE IV.

Wave length in $\mu\mu$.	Rotation in minutes.	Wave length in $\mu\mu$.	Rotation in minutes.
442·5	16·70	546·1	23·73
457·4	17·40	557·5	24·57
474·0	18·27	571·5	25·34
492·5	19·32	599·0	26·33
515·5	20·79	628·0	27·20
531·5	22·54	650·0	27·65
538·5	23·31	690·0	28·56

Rotation was always negative and the field saturated.

Iron.—(2) For this piece of material I have to thank Prof. Weiss,* of Zurich, who had determined its saturation value as s_m=216·1. The density of the material was 7·86, giving us

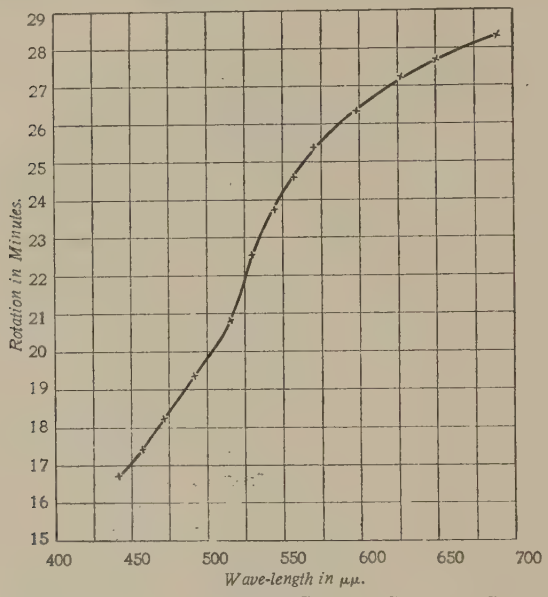


Fig. 4.—Iron (1). Dispersion Curve. Specimen Saturated.

as value for I_m=1,690 C.G.S. The specimen was free from sulphur, silicon or manganese, and had been melted in an atmosphere of nitrogen. The same process as in the previous case was gone through and the curve drawn. The results gave as the value of the abscissa of the point of intersection

$$x=4\pi I_m=21{\cdot}0 \text{ kilogauss.}$$

Therefore I_m=1,681 C.G.S.

This value is in excellent agreement with that of Prof. Weiss, the error being 9 C.G.S., or 0·5 per cent.

Iron.—(3) This specimen of Swedish iron was supplied by the Kolswa Iron Works, and contained 0·22 per cent. of carbon, phosphorus, silicon and manganese. Prof. Weiss again supplied me with his calculation of the saturation value, and gave

* P. Weiss, "Jour. de Phys." (4), p. 273, 1910.

s_m=216·5 C.G.S. The density was returned as 7·8624, and this gives as value of I_m=1,702 C.G.S.

Two sets of readings were taken, using light of different wave-lengths—namely, λ=546·1 and λ=590·1 $\mu\mu$. The saturation value obtained in both cases was the same.

TABLE V. (*a*) *and* (*b*).

Saturation curves. Iron (3). (*a*) λ=546·1 $\mu\mu$. (*b*) λ=590·1 $\mu\mu$.

Field in kilogauss.	Rotation in minutes (*a*).	Rotation in minutes (*b*).
2·89	2·88	3·40
6·00	6·09	7·06
9·60	9·77	11·43
12·40	12·25	14·82
15·43	15·17	18·43
17·51	17·05	21·08
19·67	18·32	22·26
21·71	19·05	23·10
23·37	19·78	23·73
24·91	20·25	24·23
27·07	20·46	24·50
32·65	20·48	24·99
36·18	20·59	25·13
38·08	20·59	25·13
39·70	20·59	25·13

Rotation was always negative.

The value of "x" so obtained was 20·95 kilogauss, which gives

$$I_m=\frac{20\cdot950}{4\pi}=\underline{1{,}668 \text{ C.G.S.}}$$

All further tests of the material gave values between 1,668 and 1,681 C.G.S. Taking the mean of all values found as 1,675 C.G.S. (being the mean of 25 curves), we find this in good agreement with the other value given above of 1,702 C.G.S., the error being only 1·4 per cent.

Dispersion Curve.—The dispersion curve for this specimen was found, and the results are set out in Table VI. The dispersion throughout the spectrum was fairly large, and from λ=500·0 $\mu\mu$ to λ=700·0 $\mu\mu$ the curve follows practically a straight line. The smaller values of the wave-length show a slight inflection of the curve. It is interesting to compare the values obtained in the present work with those obtained by Foote for a similar specimen. The values are compared in Table VI.(*a*), and are illustrated in Fig. 6. Table VI. gives

the results of experiment in the determination of the dispersion curve. In this case the arc lamp was not used as the source of light, but direct sunlight was focussed on to the slit of the monochromator. This additional intensity of the illumination

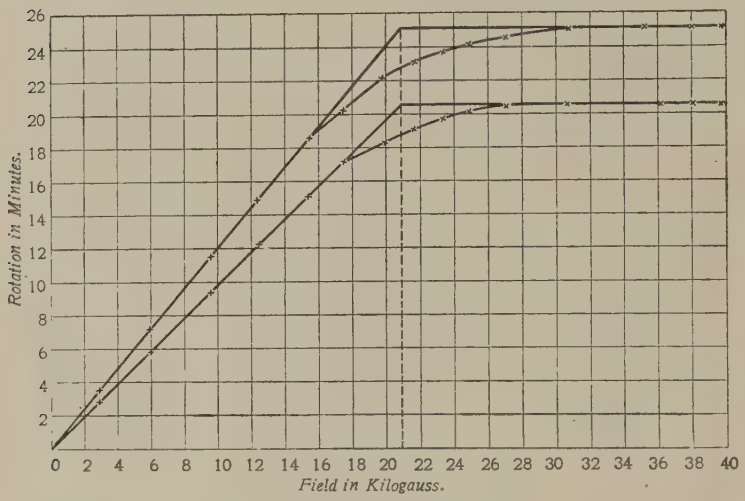


FIG. 5.—IRON (3).

Upper Curve (A) Wave-length 546, 1$\mu\mu$ (A).
Lower Curve (B) Wave-length 590, 1$\mu\mu$ (B).

enabled the readings to be taken much further into the violet than before. In all cases the maximum value of the rotation is given.

TABLE VI.

Dispersion curve. Iron (3). Field strength, 39·70 kilogauss.

Wave-length in $\mu\mu$.	Rotation in minutes.	Wave-length in $\mu\mu$.	Rotation in minutes.
435·0	14·66	531·5	20·14
442·5	14·95	538·5	20·55
457·4	15·55	546·1	20·93
465·5	15·85	571·0	22·79
478·5	16·36	599·0	24·33
492·5	17·61	650·0	27·47
504·0	18·55	690·0	29·75
515·5	19·15	...	...

The field was saturated.

TABLE VI. (*a*).—*Comparison of the Values of Barker and Foote.*

Wave-length in $\mu\mu$.	Rotation in minutes (Barker)	Rotation in minutes (Foote).	Ratio.
410·0	14·60	15·00	1·02
440·0	15·00	15·60	1·03
480·0	16·65	16·80	1·01
520·0	19·50	19·74	1·01
560·0	22·10	22·74	1·02
600·0	24·45	24·78	1·01
640·0	26·60	26·58	0·999
660·0	27·94	26·94	0·964

Taking as the mean ratio 1·01, we see that the two sets of values are in good agreement. The present work has found points further into the violet and red than that of Foote, and

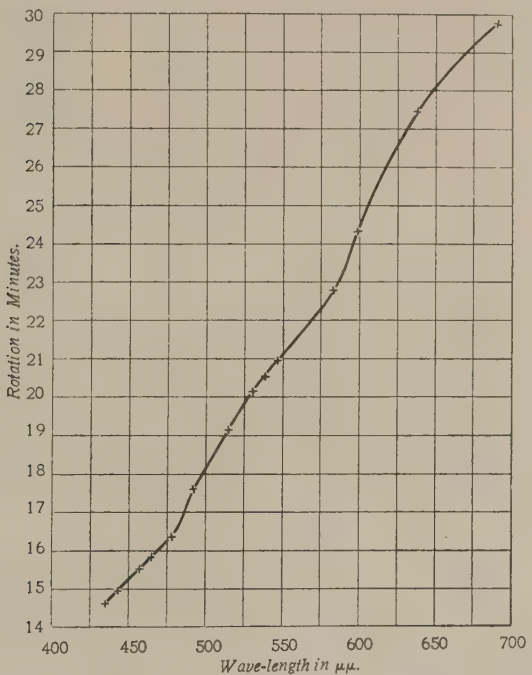


FIG. 6.—IRON (3). DISPERSION CURVE. FIELD SATURATED.

also more points were obtained. Many other specimens of iron were tested with satisfactory results.

Cobalt.

Cobalt.—(1) This specimen of electrolytic cobalt was provided by Merck, and had been fused in nitrogen. Prof. Weiss has again supplied me with the information regarding his tests of the material for the saturation value. He gave the value as 1,412 C.G.S. The piece was mounted on a cone and tested in the same way as the iron. The results are given in Table VII. and plotted in Fig. 7.

Table VII.

Saturation curve. Cobalt (1). $\lambda=530{\cdot}0\ \mu\mu$.

Field in kilogauss.	Rotation in minutes.	Field in kilogauss.	Rotation in minutes.
2·40	2·85	20·28	20·30
4·76	5·61	21·50	20·45
7·06	8·37	22·43	20·54
9·75	11·44	27·04	20·58
12·13	14·19	30·26	20·58
13·59	15·95	31·64	20·58
15·67	18·20	33·02	20·58
17·82	19·65	33·88	20·58
19·04	20·27	...	...

Rotation was negative throughout.

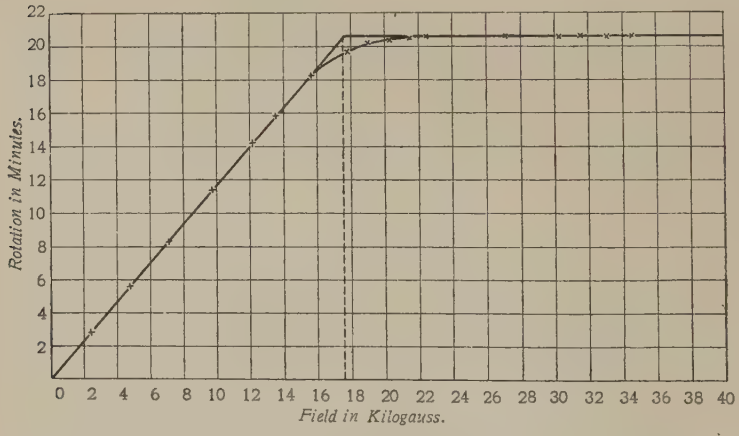


Fig. 7.—Cobalt (1). Saturation Curve. Rotation Negative.

From the curve it is seen that

$$x=4\pi I_m=17{,}600 \text{ kilogauss.}$$

Therefore $$I_m=\frac{17{,}600}{4\pi}=1{,}400 \text{ C.G.S.}$$

This value (1,400) is in excellent agreement with that of Weiss—namely, 1,412 C.G.S., the error being less than 1 per cent. The foregoing affords another example of the accuracy of the method for measuring high saturation values.

Dispersion Curve.—The dispersion curve was observed for the first time for a saturated specimen. It gave no indications of anything other than that previously observed by Martin for cobalt mirrors which were unsaturated. The definite but flat minimum in the green was more closely observed and located exactly. A great number of points were taken, and the values so obtained are set out in Table VIII. The field was maintained at 35·91 kilogauss throughout the whole experiment, and light from the arc lamp was used.

TABLE VIII.

Dispersion curve. Cobalt (1). Field strength, 35·91 kg.

Wave-length in $\mu\mu$.	Rotation in minutes.	Wave-length in $\mu\mu$.	Rotation in minutes.
442·5	23·60	546·1	22·36
457·2	23·37	571·5	22·59
492·5	22·80	599·0	22·96
515·5	22·45	618·0	23·24
525·0	22·31	650·0	23·68
531·5	22·30	690·0	24·25
538·5	22·30	...	...

Rotation was negative throughout.

The values given above bear an interesting comparison with those obtained by Martin. If his results be multiplied by the factor 1·134 the above curve is obtained. The curve is shown

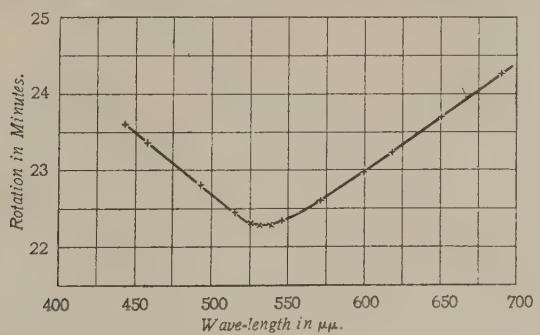


FIG. 8.—COBALT (1). DISPERSION CURVE. ROTATION NEGATIVE.

in Fig. 8. Table VIII.(*a*) gives the comparison of Martin's values with those above.

TABLE VIII. (*a*).

Wave-length in $\mu\mu$.	Rotation in minutes (Barker).	Rotation in minutes (Martin).	Ratio.
483·0	22·95	20·20	1·131
530·0	22·30	19·74	1·130
567·0	22·65	19·92	1·137
615·0	23·20	20·28	1·139
675·0	24·00	21·15	1·135

Allowing for the fact that the Martin observations were taken with an unsaturated mirror and in this case it was saturated, the agreement is good throughout.

Cobalt.—(2) Another specimen was similarly tested and was supplied to me through the kindness of Prof. Merrett from the Metallurgical Department of the Imperial College, London. It was considered tolerably pure. The whole apparatus was maintained as before. The value so obtained from the curve was 1,395 C.G.S., which is again in good agreement with Weiss' result for cobalt. Other specimens were tested and gave equally satisfactory results.

NICKEL.

Nickel.—(1) This piece was originally supplied by Merck and afterwards fused in nitrogen by Weiss. Prof. Weiss gave as its saturation value 490 C.G.S. The mirror was prepared and tested in the same way as before, and the curve followed

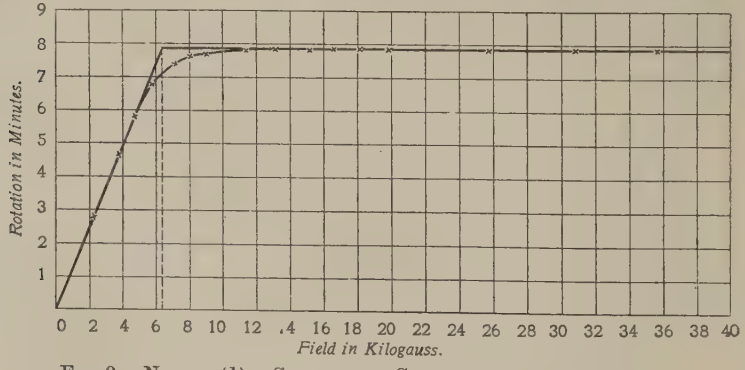


FIG. 9.—NICKEL (1). SATURATION CURVE. ROTATION NEGATIVE.

the usual form. The results of experiment are shown in Table IX.

TABLE IX.

Saturation curve. Nickel (1). $\lambda=590{\cdot}0\ \mu\mu$.

Field in kilogauss.	Rotation in minutes.	Field in kilogauss.	Rotation in minutes.
2·38	2·81	11·40	7·80
3·80	4·60	13·21	7·85
4·76	5·72	15·05	7·85
5·70	6·75	16·66	7·85
7·10	7·35	18·16	7·85
8·00	7·60	*19·28	7·85
9·20	7·65	...	...

* All readings were constant for higher fields.

From the curve, Fig. 9, we see that

$$x=4\pi I_m=6{,}400 \text{ kilogauss.}$$

Therefore $$I_m=\frac{6{,}400}{4\pi}=509 \text{ C.G.S.}$$

This value is a little higher than those before obtained, but still the difference is less than 4 per cent. The process of soldering to the cone might have had a little influence in raising the value. The method is therefore good for substances of weaker magnetisation.

Disperison Curve.—Great care was taken to determine the exact form of the dispersion curve, and more than twice as many points as found by Foote were taken. The curve agrees remarkably well with his. A well-defined flat minimum was found in the region from $\lambda=530{\cdot}0\ \mu\mu$ to $\lambda=550{\cdot}0\ \mu\mu$, and a maximum was observed at $\lambda=600{\cdot}0\ \mu\mu$, coming again to a minimum at $\lambda=630{\cdot}0\ \mu\mu$. These irregularities were very carefully observed, and the results were determined with great accuracy. Table X. gives the values found.

TABLE X.

Dispersion curve. Nickel (1). Field strength, 31·40 kg.

Wave-length in $\mu\mu$.	Rotation in minutes.	Wave-length in $\mu\mu$.	Rotation in minutes.
442·5	8·316	557·5	7·196
457·2	8·092	571·5	7·40
474·0	7·80	599·0	8·05
492·5	7·52	618·0	7·90
515·5	7·32	628·0	7·75
531·5	7·21	650·0	8·076
539·0	7·21	690·0	8·230
546·1	7·21	...	...

The nickel was saturated and a field of 31·400 kilogauss was maintained throughout.

Nickel.—(2) This piece was supplied as tolerably pure nickel from the Metallurgical Department of the Imperial College, London, by Assistant Prof. Merrett. It was duly tested as before and gave as maximum rotation 8·05 minutes. From

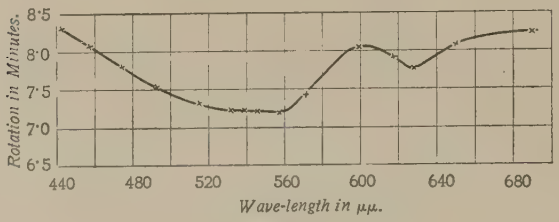


Fig. 10.—Nickel (1). Dispersion Curve. Rotation Negative.

the curve obtained x was found to be equal to 6,450 gauss, and this gives as value of I_m or the saturation value equal to 513 C.G.S. This result is in accordance with the one previously obtained for Nickel (1). Other specimens of nickel were examined and gave consistent results of a like order.

The method having thus far been tested for ferro-magnetic metals, it was next applied to alloys of the same. By the kindness of Dr. Gumlich, of the Physische Technische Reichsanstalt, Berlin, specimens of ferro-manganese alloys of known saturation values were obtained. Concordant results were again found and the results are set out below.

Alloys.

Ferro-Manganese.—(1) This specimen was kindly supplied by Dr. Gumlich, and had the percentage composition—

Iron=92·2 per cent.

Manganese= 7·8 per cent.

Dr. Gumlich gave as the saturation value 1,360 C.G.S. With light of wave-length λ=530·0 $\mu\mu$, the maximum rotation was found to be 19·70 minutes, and throughout the whole experiment was in the negative direction. Table XI. gives the values obtained for the saturation curve.

TABLE XI.

Saturation curve. Ferro-Manganese (1). $\lambda=530{\cdot}0\ \mu\mu$.

Field in kilogauss.	Rotation in minutes.	Field in kilogauss.	Rotation in minutes.
2·536	3·0	19·320	18·83
4·000	4·7	21·980	19·60
4·602	5·4	23·560	19·70
5·323	6·2	24·090	19·70
7·399	8·8	26·080	19·70
8·303	9·8	31·660	19·70
9·745	11·5	35·330	19·70
11·820	14·0	37·000	19·70
14·890	16·63	39·070	19·70
17·510	18·34	39·610	19·70

The rotation was negative.

From the curve so obtained (Fig. 11) we find that

$$x=4\pi I_m=16{,}750 \text{ kilogauss.}$$

Therefore $$I_m=\frac{16{,}750}{4\pi}=1{,}333 \text{ C.G.S.}$$

This is in excellent agreement with the value given by Gumlich (1,360), the error being less than 2 per cent.

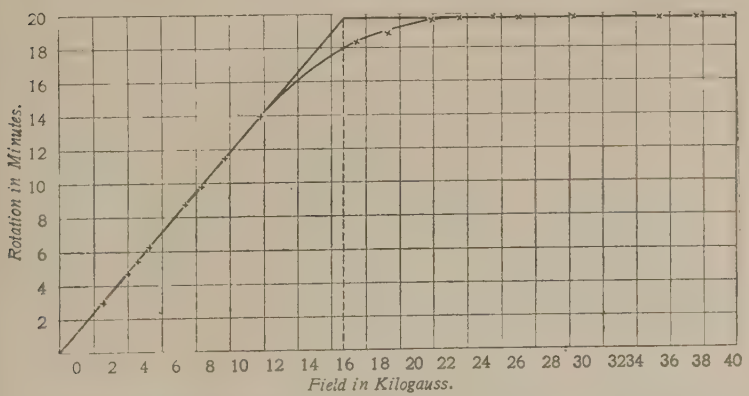


FIG. 11.—FERRO-MANGANESE (1). SATURATION CURVE. ROTATION NEGATIVE.

Ferro-Manganese.—(2) This specimen was also supplied by Dr. Gumlich, and was a piece which he had himself tested by the isthmus method. The usual mirror was prepared and

mounted in the large Du Bois magnet as before. The composition of the piece was given by Gumlich as

Iron=89·6 per cent.

Manganese=10·4 per cent.

Light of wave-length $\lambda=530{\cdot}0\ \mu\mu$ was used, the same as in the case of specimen (1). The maximum rotation fell from 19·70

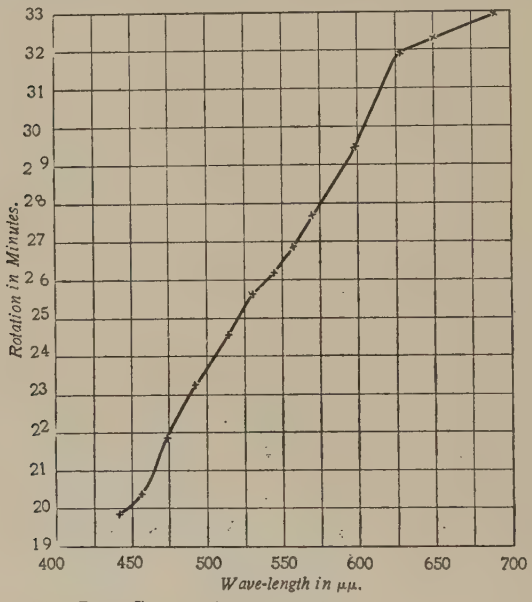


Fig. 12.—Iron-Cobalt Antimony Alloy. Dispersion Curve.

to 13·16 minutes. This shows that the introduction of 2·6 per cent. more manganese had the effect of considerably diminishing the rotation. As before, the rotation was negative. From the curve obtained it was seen that

$$x=4\pi I_m=10{,}970 \text{ kilogauss.}$$

Therefore $$I_m=\frac{10{,}970}{4\pi}=873 \text{ C.G.S.}$$

Dr. Gumlich gave his value as 885 C.G.S., and by comparison of figures the close agreement of the two methods is readily seen, the error being less than 1·4 per cent.

The foregoing examples are sufficient to demonstrate the efficacy of the method for measuring saturation values of highly magnetic substances. In this case the error from other recognised methods is never more than 2 per cent. When bodies of less magnetic power are tested, then the error is perhaps a little greater, but in no case greater than 4 per cent. The apparatus was now used to determine the saturation values of bodies hitherto untested, and which in many cases could only be obtained in small quantities. In all cases mirrors were prepared as before and highly polished. In some few cases the dispersion curves were also determined. According to the results obtained above the differences between the experimental values and those obtained from the theory of Du Bois are very small. With regard to bodies of low magnetic value, the possible reduction of the percentage error is occupying my attention, and already more accurate readings have been obtained. In the cases below, where the saturation value is below 500 C.G.S., the results can be regarded as correct to within 3 per cent., whilst for bodies of higher values 1 per cent., or at the most 1·5 per cent., is the limit of error.

Ferro-Cobalt-Antimony.—This alloy was supplied from the collection of Prof. Du Bois, and contained

Iron=66 per cent.
Cobalt=30 per cent.
Antimony= 4 per cent.

Using light of wave-length $\lambda=530{\cdot}0\ \mu\mu$, a maximum rotation of 23·66 minutes was obtained in the negative direction. The curve followed the usual form.

The value found for x on plotting the values obtained was

$$x=4\pi I_m=19{,}600 \text{ kilogauss.}$$

Therefore $$I_m=\frac{19{,}600}{4\pi}=\underline{1{,}607 \text{ C.G.S.}}$$

An alloy of these three metals gives, therefore, a high saturation value. The dispersion curve was also determined for this specimen and the result is set out in Table XII.

TABLE XII.

Dispersion curve. Alloy Fe-Co-Sb. Field = 32·94 kg.

Wave-length in $\mu\mu$.	Rotation in minutes.	Wave-length in $\mu\mu$.	Rotation in minutes.
442·5	19·74	557·5	26·81
457·4	20·33	571·5	27·68
474·0	21·81	599·0	29·43
492·5	23·24	628·0	31·92
515·5	24·57	650·0	32·30
531·5	25·65	690·0	32·52
546·1	26·18	...	...

Rotation is negative.

The curve is quite regular, and shows a steady increase from $\lambda=440$ $\mu\mu$ to $\lambda=610{\cdot}0$ $\mu\mu$. After this point is reached it bends sharply and shows a very small increase from $\lambda=610$ $\mu\mu$ to $\lambda=700$ $\mu\mu$. There is a tendency towards a minimum value in the violet and towards a maximum in the red.

Ferro-Cobalt.—This was given me by Prof. Weiss, and was stated to be a compound of the formula Fe_2CO. It was the outcome of a fusion of the two metals by Weiss and von Freudenreich. Using $\lambda=530{\cdot}0$ $\mu\mu$, the maximum negative rotation was found to be 27·64 minutes. The curve obtained gave x equal to 23·300 kilogauss, and this furnishes us with a saturation value of 1,850 C.G.S. Both the rotation and the saturation values found were high.

Ferro-Nickel.—This was also kindly supplied by Prof. Weiss from the same source as the ferro-cobalt. It had the definite composition shown by the formula Fe_2Ni. The material gave an excellently polished mirror, and using light of wave-length $\lambda=530{\cdot}0$ the maximum negative rotation was found to be equal to 15·05 minutes. The results are shown in Table XIII.

TABLE XIII.

Saturation curve. Ferro-Nickel. $\lambda=530{\cdot}0$ $\mu\mu$.

Field in kilogauss.	Rotation in minutes.	Field in kilogauss.	Rotation in minutes.
2·436	3·28	10·74	13·86
3·835	5·40	12·81	14·56
5·234	7·20	15·52	14·86
7·038	9·68	17·14	15·05
8·121	11·21	19·13	15·05
9·204	12·50	...	...

Rotation is negative. Rotation is constant for all higher fields.

This curve, when plotted as in Fig. 13, gives $x=11{\cdot}00$ kilogauss, and this gives as the saturation value $I_m=875$ C.G.S.

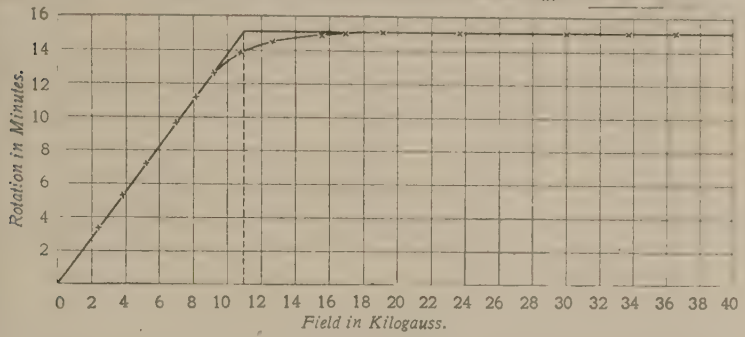


FIG. 13.—FERRO-NICKEL. SATURATION CURVE. ROTATION NEGATIVE.

Cobalt-Silicon.—This alloy was prepared at the Metallurgical Laboratory of the Imperial College, London, by kind permission of Asst. Prof. Merrett. It had the percentage composition—

Cobalt=98 per cent.
Silicon= 2 per cent.

Using light of wave-length $\lambda=530{\cdot}0\ \mu\mu$, a maximum negative rotation was attained of 20·52 minutes. A regular curve was given, and the point of intersection showed $x=13{\cdot}80$ kilogauss. Thus we have as the saturation value

$$I_m=1{,}094 \text{ C.G.S.}$$

Cobalt-Chromium.—The specimen was prepared as above in London and had the composition—

Cobalt=87 per cent.
Chromium=13 per cent.

With all conditions as before, the substance gave a maximum negative rotation of 13·72 minutes. From the graph so obtained x was found to be equal to 11·22 kilogauss, given as the saturation value

$$I_m=880 \text{ C.G.S.}$$

Cobalt-Chromium-Nickel.—Prof. Tammann, of the University of Gottingen, sent me the piece tested, and kindly gave me the analysis of its composition as

Cobalt=83 per cent.
Chromium=15 per cent.
Nickel= 2 per cent.

The curve was of the usual order, and gave a negative maximum

rotation of 8·96 minutes. By deduction therefrom the value of $x=9{\cdot}75$ kilogauss, which renders the value of $I_m=775$ C.G.S. The wave-length used was $\lambda=530{\cdot}0\ \mu\mu$.

Cobalt-Tin.—The specimen was fused in the Metallurgical Laboratory of the Imperial College, London, and on analysis had the percentage composition—

Cobalt=93·2 per cent.
Tin= 6·8 per cent.

The mirror was prepared and tested as before, and with light of wave-length $\lambda=530{\cdot}0\ \mu\mu$ gave a negative maximum rotation of 14·3 minutes. The curve presented an abnormal appearance, insomuch that the transition portion is almost evanescent and the saturation point is almost reached before the bend occurs. The turn is very sharp and very small in gradient. The results are set out in Table XIV.

TABLE XIV.

Saturation curve. Cobalt-Tin. $\lambda=530{\cdot}0\ \mu\mu$.

Field in kilogauss.	Rotation in minutes.	Field in kilogauss.	Rotation in minutes.
2·526	2·48	13·90	14·14
3·900	3·87	16·06	14·21
5·500	5·47	18·95	14·24
7·210	7·19	19·86	14·28
8·480	8·49	21·39	14·30
9·920	9·98	22·92	14·30
11·370	11·30	...	...

The rotation remained constant at 14·3 minutes for all higher values of the magnetic field. Rotation was negative.

From the above figures, when plotted in Fig. 14, the value of x is estimated as $x=14{\cdot}19$ kilogauss.

Therefore $I_m=1{,}129$ C.G.S.

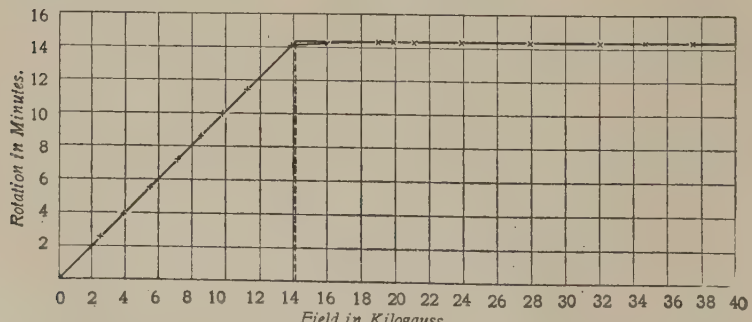


FIG. 14.—COBALT-TIN. SATURATION CURVE. ROTATION NEGATIVE.

A specimen of a cobalt-tin alloy which had been tested five years previously, and found to be magnetic, by Martin, was re-tested by Martin after three years and gave no rotation. The specimen was re-tested in the present work—*i.e.*, two years later—and again gave no result. It was then maintained at a temperature of 100 deg. Centigrade for two days and re-tested. Again a negative result was obtained. It was apparent, therefore, that in the five years some change had taken place in the alloy. The piece tested in Table XIV. is almost identical in composition with the original of Martin. This apparent ageing of the alloy we have been unable to explain up to date.

Cobalt-Antimony.—The material was prepared in London by the kindness of Prof. Merrett, of the Imperial College, who gave its percentage composition as

Cobalt=88 per cent.
Antimony=12 per cent.

The usual curve was obtained, with light of wave-length λ =530·0 $\mu\mu$, and it presented no peculiarities. The maximum negative rotation was 18·72 minutes, and the value of x found was 14·50 kilogauss. The saturation value deduced from this gives

$$I_m = 1{,}155 \text{ C.G.S.}$$

MINERALS, &c.—*Magnetite*, FeO, Fe_2O_3. *Magnetite* (1), (2) and (3).

General Remarks.—According to the curves for dispersion obtained by Loria and Martin in the case of magnetite, there is a negative rotation in the blue about wave-length λ=450·0 $\mu\mu$ and a positive rotation in the orange-red about wave-length λ=600·0 $\mu\mu$. In all cases where the saturation value of this substance was found two curves were taken using light of wave-lengths λ=450·0 $\mu\mu$ (blue) and λ=600·0 $\mu\mu$ (orange-red). In the first case the rotation was negative, and a slit width of 0·30 mm. was used on the monochromator. In the second case the rotation was negative and the slit width was decreased to 0·15 mm.

Magnetite.—(1) This specimen was taken from the end of an electrode and mounted in the usual way. Using light of wave-length λ=450·0, the maximum negative rotation obtained was 1·89 minutes, and using light of wave-length λ=600·0 $\mu\mu$, the

maximum positive wave-length was 3·83 minutes. Both curves gave exactly the same value for x—namely,

$x=5{\cdot}190$ kilogauss, which gives $I_m=413$ C.G.S.

Magnetite.—(2) This specimen was kindly provided by Prof. Weiss, who stated that it had been artificially prepared. It was in an amorphous condition, and so had to be compressed strongly on to the cone prepared for insertion into the pole-piece of the magnet. In this way a mirror with a fairly good polish was obtained. Using the two wave-lengths as before, two good curves were traced. With wave-length $\lambda=450{\cdot}0\ \mu\mu$ the maximum negative rotation was 1·10 minutes, and using wave-length $\lambda=600{\cdot}0\ \mu\mu$ the maximum positive rotation was 2·25 minutes. Again both curves gave identical values for x—viz.,

$x=5{\cdot}100$, and therefore $I_m=406$ C.G.S.

The two results are in good agreement.

Magnetite.—(3) This was a piece of natural mineral taken from the collection of Prof. H. du Bois. It was carefully mounted, as in the case of the earlier specimens, and the tests applied, using light of two wave-lengths as before. The curve obtained using light of wave-length $\lambda=450{\cdot}0\ \mu\mu$ gave a maximum negative rotation of 2·0 minutes, and the maximum positive rotation obtained with light of wave-length $\lambda=600{\cdot}0\ \mu\mu$ was 3·20 minutes.

The results of the two tests are set forth in Table XV. (*a*) and (*b*), and are traced in Figs. 15 and 16. The upper curve is the positive one.

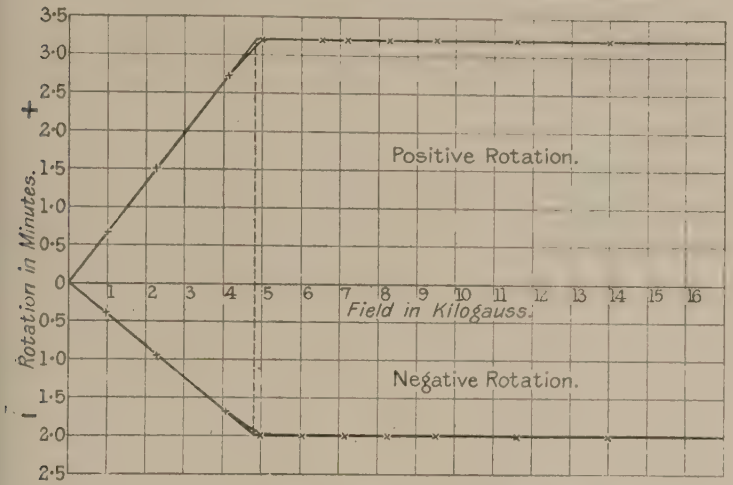
TABLE XV. (*a*) *and* (*b*).

Saturation curves. Magnetite (3). (*a*) $\lambda=450{\cdot}0\ \mu\mu$. (*b*) $\lambda=600{\cdot}0\ \mu\mu$.

Field in kilogauss.	$\lambda=450{\cdot}0\ \mu\mu$ rotation in minutes (negative).	$\lambda=600{\cdot}0\ \mu\mu$ rotation in minutes (positive).
1·00	0·40	0·675
2·30	0·95	1·50
4·10	1·70	2·75
4·95	2·00	3·20
6·55	2·00	3·20
7·20	2·00	3·20
8·25	2·00	3·20
9·50	2·00	3·20
11·60	2·00	3·20

For all higher values of the field the rotations were constant.

Figs. 15 and 16 both show the same value for x—namely, the value of $x=4{\cdot}850$ kilogauss, therefore I_m 383 C.G.S.



FIGS. 15 AND 16.—MAGNETITE (1). SATURATION CURVES.

Franklinite (ZnO, Fe_2O_3).—This specimen was also loaned by Prof. du Bois from his collection, and had the composition as expressed by the formula above. In order to select a suitable wave-length for the determination of the saturation curve, it was necessary to first determine the dispersion curve.

TABLE XVII.

Franklinite. Dispersion curve. Field = 27·34 kg.

Wave-length in $\mu\mu$.	Rotation in minutes.	Wave-length in $\mu\mu$.	Rotation in minutes.
442·5	−1·40	557·5	+0·78
457·4	−1·26	571·5	+0·92
474·0	−1·09	599·0	+0·98
492·5	−0·65	628·0	+1·05
515·5	+0·00	650·0	+1·12
531·5	+0·30	690·0	+1·19
546·1	+0·42	...	...

The procedure was just as usual, and the curve obtained very interesting. It commenced with a negative incline and passed through a zero value at $\lambda=515{\cdot}5\ \mu\mu$. After this it made a slight dip on the positive side, and then bent sharply round at

λ=570·0 $\mu\mu$. The curve then increased slowly towards the higher values of the wave-length. Throughout the whole experiment the field was saturated and maintained at 27·34 kilogauss. Table XVII. and Fig. 17 show the results.

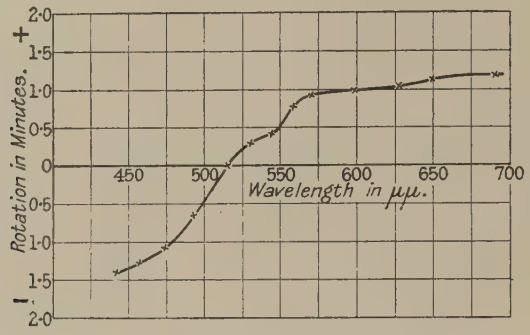


Fig. 17.—Franklinite. Dispersion Curve. Rotation Negative and Positive.

Saturation Curve.—From the foregoing curve it was thought best to select a wave-length of λ=450·0 $\mu\mu$ for the determination of the saturation curve. This entailed a monochromator

Table XVIII.

Saturation curve. Franklinite. λ=450·0 $\mu\mu$.

Field in kilogauss.	Rotation in minutes.	Field in kilogauss.	Rotation in minutes.
0·8	0·5	3·7	1·19
1·1	0·7	4·9	1·19
1·7	1·1	5·8	1·19
2·85	1·19	7·5	1·19

Rotation is constant for all higher field values.

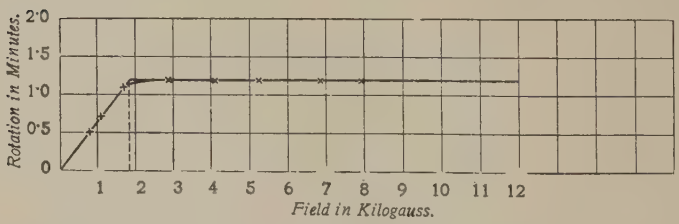


Fig. 18.—Franklinite. Saturation Curve. Rotation Negative.

slit width of 0·3 mm., and the rotation was negative throughout the whole curve. The results obtained are set out below in Table XVIII, and the curve shown in Fig. 18.

Fig. 15 gives the value of x—

$$x = 1{\cdot}870 \text{ kilogauss.}$$

Therefore $I_m = 149$ C.G.S.

Cupri-ferrite (CuO, Fe_2O_3).—This specimen was supplied as before by Prof. du Bois, and had the composition represented by the formula above. According to previous workers, it gave a positive rotation, and taking a monochromator slit width of 0·3 mm., light of wave-length $\lambda = 477{\cdot}0$ $\mu\mu$ was used for the curve. The usual series of values was obtained and Table XIX. gives the results.

TABLE XIX.

Cupri-ferrite. Saturation curve. $\lambda = 477{\cdot}0$ $\mu\mu$.

Field in kilogauss.	Rotation in minutes.	Field in kilogauss.	Rotation in minutes.
0·75	+0·4	4·1	+1·65
1·2	+0·6	5·15	+1·68
1·9	+0·95	7·50	+1·68
3·1	+1·55	...	...

Rotation is positive and is constant for all higher field values.

The curve quickly attains its maximum, and from it we find the value of

$$x = 3{\cdot}350 \text{ kilogauss,}$$

which gives $I_m = 266$ C.G.S.

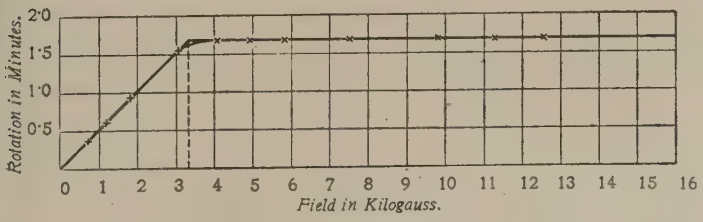


FIG. 19.—CUPRI-FERRITE. SATURATION CURVE. ROTATION POSITIVE.

In the final table are set out the whole of the values found by this method. The reliability of it is well proved in the first cases tested, and, as mentioned before, it is particularly good when only small quantities of the materials to be tested are available. In conclusion, I should like to thank most heartily Prof. H. du Bois, of Amsterdam and Berlin, for so kindly placing his apparatus and advice at my disposal for the work,

Prof. Weiss, of Zurich, Dr. Gumlich, of Berlin, Asst. Prof. Merrett, of London, for so generously providing me with specimens, and Mr. J. Stephenson, A.R.C.Sc., B.Sc., for help during the writing of this Paper.

Material.	Maximum rotation in minutes.	Saturation value found in C.G.S.	Wave-length used in $\mu\mu$.	Otherwise found saturation value in C.G.S.	Source of material.	Rem
Iron (1)	−22·68	1,681	530·0	1,705	Gumlich	
Iron (2)	−18·97	1,681	530·0	1,690	Weiss	Fuse ni
Iron (3)	−20·59 −25·13	1,675	546·1 590·1	1,702	Kolswa	Swed
Cobalt (1)	−20·58	1,400	530·0	1,412	Weiss	Fuse nit
Cobalt (2)	−21·00	1,395	530·0	1,406	Merrett	
Nickel (1)	− 7·85	509	590·0	490	Weiss	
Nickel (2)	− 8·05	513	530·0	...	Merrett	
Ferro-Manganese (1)	−19·70	1,333	530·0	1,360	Gumlich	Fe = Mn =
Ferro-Manganese (2)	−13·60	873	530·0	885	Gumlich	Fe = Mn =
Iron-Cobalt-Antimony.	−23·66	1,607	530·0	...	Du Bois	Fe = Co = Sb =
Ferro-Cobalt	−27·64	1,850	530·0	...	Weiss	Fe_2C
Ferro-Nickel	−15·05	875	530·0	...	Weiss	Fe_2N
Cobalt-Silicon	−20·52	1,094	530·0	...	London	Co = Si =
Cobalt-Chromium	−13·72	880	530·0	...	London	Co = Cr =
Cobalt-Chromium-Nickel.	− 8·96	775	530·0	...	Tammann	Co = Cr = Ni =
Cobalt-Tin	−14·30	1,129	530·0	...	Merrett	Co = Sn =
Cobalt-Antimony	−14·50	1,155	530·0	...	Merrett	Co = Sb =
Magnetite (1)	−1·89 +3·83	413	450·0 600·0	...	Electrode	FeO.
Magnetite (2)	−1·10 +2·25	406	450·0 600·0	...	Weiss	As ab
Magnetite (3)	−2·00 +3·20	383	450·0 600·0	...	Du Bois	As ab
Franklinite	−1·19	149	450·0	...	Du Bois	ZnO.
Cupri-Ferrite	+1·68	266	477·0	...	Du Bois	CuO.

ABSTRACT.

The Paper describes work carried out in the laboratory of Prof. Du Bois on the relation between the intensity of magnetisation of various ferro-magnetic materials and the rotation of the plane of polarisation of plane polarised light reflected from a polished surface of the material. The specimens, in the form of circular discs 5 mm. in diameter and 0·5 mm. thick, were soldered to one of the pole pieces of a large electromagnet. Through an aperture in the other pole, monochromatic light, polarised in two nearly coincident planes by means of a Lippich polariser, was incident almost normally on the polished surface of the specimen. The reflected beam passed through an analyser, the rotation of which could be measured, by means of an auxiliary optical system, to a high degree of accuracy.

In the first part of the Paper results are given for a number of materials of known magnetic properties in order to establish the validity of the method, due to Du Bois, of obtaining the value of the saturation intensity from the curve connecting field strength with rotation. The method is then applied to materials of unknown properties. The variation of the Kerr constant with the wave-length of the light was also determined for a number of substances.

DISCUSSION.

Mr. D. Owen asked if the Paper, in addition to establishing the view that the rotation was proportional to the intensity of magnetisation, brought forward any new results that were useful to theory. For instance, he recollected a Paper by B. Hopkinson, in which it was found possible to obtain an intensity of magnetisation greater than that obtainable with pure iron, and he noticed that in the present Paper there was an alloy of iron and cobalt which exceeded pure iron in saturation intensity. Was it now taken for granted that it was possible in an alloy to obtain magnetisations greater than that of either component, or were the results in the Paper somewhat novel in this respect ?

Dr. Smith said that saturation intensities of magnetisation were of importance for various reasons. For instance, as Weiss had shown, it was of theoretical interest to know their temperature variations. Again, in the case of a " mechanical " mixture of two substances, the saturation intensity would be related in a simple manner to those of the constituents. There was much evidence that annealed steels are mixtures of iron and iron carbide. Hadfield and Hopkinson, in the Paper which had been mentioned, had shown that the saturation intensities of magnetisation of such steels were compatible with this view, and had deduced a value for the saturation intensity of the carbide. It would have been of interest if Dr. Barker had determined the latter directly, as had been his intention, before the work was interrupted. Alloys were not, however, always simple mixtures. The steel examined by Hopkinson and Hadfield to which Mr. Owen had referred, was a nickel steel, and its total magnetisation was greater than the sum of those which its constituents would have exhibited separately, although it was not as great as that of pure iron. The reason probably was that nickel-iron alloys form solid solutions (mixed-crystals) instead of mechanical mixtures. The same is probably true of cobalt-iron alloys, although in this case a material can be obtained (possibly a compound) whose saturation magnetisation is actually greater than that of pure iron. It had been proposed to use this alloy commercially. Other solid solutions were known in some of which

the magnetisation was greater, and in others less, than that which mechanical mixtures of the components would have exhibited.

Dr. P. E. Shaw (communicated remarks): The peculiar features of the interesting method employed by Dr. Barker are the smallness of the specimens and the largeness of the field used. In order to obtain rotation effects of fair magnitude it would seem to be necessary to deal exclusively with magnetic materials of ferromagnetic strength, and even then to employ great fields. This limitation in the scope of the method is, however, counterbalanced by the great advantage of being able to experiment on very small quantities of the magnetic substance. It would thus seem easy to conduct useful experiments on the change in magnetic quantity of the small specimens when the conditions as to temperature, annealing and static treatment are varied, all of which tests might be difficult with large specimens. Throughout the Paper the values of λ are given in terms of $\mu\mu$. The unit here meant is one-millionth of a millimetre, which is now, according to recent changes in nomenclature, styled $m\mu$. The Society recently sanctioned this change.

II. *The Influence of the Time Element on the Resistance of a Solid Rectifying Contact.* *By* DAVID OWEN, *B.A., B.Sc., Birkbeck College and Borough Polytechnic Institute, London.*

RECEIVED OCTOBER 2, 1916.

THE properties of a rectifying contact may be studied by examining the curve connecting its resistance with the value of the steady applied voltage. In a previous Paper* some examples of such curves, or resistance characteristics, were given, and from its properties an expression was found for the sensitiveness of the contact treated as a rectifier of high-frequency oscillatory currents. It is, however, an obvious experimental fact that the resistance of a contact depends appreciably on the time of application of the voltage. Considerable definiteness is secured by applying the testing voltage for a small fraction of a second. The form of the characteristic determined in this manner is, moreover, explicable in terms of simple thermo-electric considerations. Experiments since carried out with the object of more fully determining the influence of the time element form the subject-matter of the present Paper.

The results have a bearing in the first place on the calculation, above alluded to, of the sensibility of a wireless receiving circuit including the contact. They have a further interest in their bearing on the thermo-electric theory of the contact; in connection with which arises the question of the location to be ascribed to the thermal effects which (on this theory) accompany and give rise to the observed variations of electric resistance.

The conclusion is reached that there is present at the interface of the contact a stratum of molecular thickness in which resides a considerable proportion of the total resistance of the contact; and that it is only the changes occurring within this stratum that are capable of causing rectification at frequencies such as are used in wireless telegraphy.

The subject of the time-lag of resistance at a contact has been previously examined by Pierce,† who, in experiments made with alternating currents of 80 $\sim$ was unable to detect the existence of any lag. From the observations recorded below it follows that such a lag is necessarily present, though

* "Proc. Ph. Soc., London," Vol. XXVIII., p. 173, June, 1916.

† "Phys. Rev.," 1907.

not to an extent which would be probably appreciable in cathode ray oscillograms taken under the conditions of the experiments quoted.

The Method of Measurement.

The Wheatstone Bridge was again employed. It is required to measure the resistance of a contact at a known time, which may be a small fraction of a second, after completing the battery circuit. When the time is a second, or more, the ordinary method of obtaining a balance can, of course, be employed. For the shorter times a ballistic method was substituted. The galvanometer key being closed, the battery circuit is closed for the period determined upon; the process being repeated until, by adjustment of the variable arm, the galvanometer throw is reduced to zero.

Two methods of making the battery circuit were used. For the shortest periods—from $\frac{1}{40000}$ second to $\frac{1}{200}$ second—the circuit was closed by allowing a polished metal ball or ring suspended by a fine wire to strike the filed and polished surface of a heavy piece of steel plate. The duration of the collision depends on the ball or ring used, and to a slight extent on the distance of its withdrawal from the plate before release. This time was independently ascertained by measuring the charge communicated, during the collision, to a mica condenser in series with a resistance of known and suitable value. The data thus obtained are given below :—

TABLE I.—*Periods of Collision.*

No.	——	——
1	Steel bicycle ball, diameter 0·71 cm.	0·000025 second
2	Brass sphere, diameter 2·54 cm.	0·00012 ,,
3	Brass sphere, diameter 5·1 cm.	0·00026 ,,
4	Brass ring, diameter 5·0 cm.	0·00036 ,,
5	Brass ring, diameter 10·0 cm.	0·00082 ,,
6	Brass sphere, diameter 21 7 cm.	0·00112 ,,
7	Manganin wire ring, diameter 10 cm.	0·0031 ,,

At the shortest periods the difficulty naturally arises of maintaining the sensibility of the bridge. A Broca galvanometer of 1,000 ohms was employed, and the bridge was arranged to give as far as possible maximum sensibility. The sensibility was then increased by repeating the collision a number of times in rapid succession. It was found that this could be done satisfactorily by hand. The ball was first soldered to a suitably stiff wire which was then insulated with

silk and used as a handle. It is possible in case of the bicycle ball to strike the steel plate some five or six times per second. Since the period of the galvanometer needle was about 10 seconds, one could use with effect some 15 strokes, thereby gaining an increase in the accuracy of measurement in nearly that proportion. In this way it was found that a resistance of 1,200 ohms was measurable to within one ohm when the period of closure of the battery circuit was 0·000025 second, the voltage applied to the bridge being 2 volts. Since the interval between successive strokes is about one-fifth of a second, a time very large compared with the duration of one contact, the e is no doubt that the resistance which the operation furnishes is that corresponding to a single stroke.

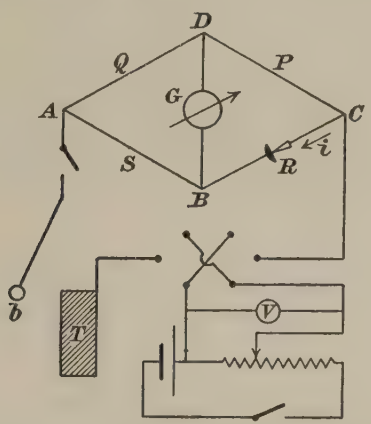


FIG. 1.—DIAGRAM OF BRIDGE FOR BALLISTIC TEST.
The battery circuit is momentarily completed by allowing the ball or ring *b* to collide with the metal plate *T*.

This collisional method becomes inconvenient when the time of contact required is greater than about 0·005 second. For times ranging between 0·005 second and 0·5 second a revolving disc of wood of diameter 14 cm. was used, into the periphery of which were let several sectors of brass of differing size. Metallic connection could be made between any one of these and the spindle, which was of gun-metal. Circuit was completed through brass brushes. The disc could be driven uniformly at any speed between 50 and 150 revs. per min. It is easy by means of a simple key to confine observations to the effect of a single closure of the circuit. The electrical connections of the bridge are shown in the diagram of Fig. 1.

Theory of the Ballistic Bridge.—When one of the four arms of a Wheatstone Bridge contains a resistance which varies during the period of application of the voltage, it is evidently impossible to find a balance in the sense that no current whatever flows in the galvanometer branch. It is possible, however, to adjust the variable arm so that the total quantity of electricity passing through the galvanometer is zero.

Let R denote the instantaneous resistance of the contact under test; P, Q and S, the resistances of the remaining arms; and G the resistance of the galvanometer. The resistance of the battery branch may be kept negligibly small; this results in some simplification in the theory. Let

V=voltage across bridge (A to C),

v=instantaneous voltage across R (B to C),

i=instantaneous current through R,

t=time from instant of closure of battery circuit.

τ=total period of closure of circuit,

$\bar{v}$ and $\bar{i}$ denote mean values of v and i over the time t.

Applying Kirchhoff's equations, and observing the condition that the integral flow of electricity through the galvanometer is zero, we have at balance

$$\frac{P}{Q}=\frac{\int Ridt}{\int Sidt}=\frac{\int vdt}{S\int idt}=\frac{\bar{v}}{S\bar{i}} \quad . \; . \; . \; ;$$

therefore

$$\frac{P}{Q}.S=\frac{\bar{v}}{\bar{i}}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Again

$$\bar{v}=V-S\bar{i}=V.\frac{P}{P+Q}; \quad . \; . \; . \; . \; . \; . \quad (2)$$

whence

$$\bar{i}=\frac{VQ}{S(P+Q)}. \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

It will be seen that $\bar{v}$ and $\bar{i}$ are at once calculable in terms of V and the resistances of the three known arms.

From a series of measurements with different values of τ a curve can be drawn connecting $\bar{i}$ and t. From this may be determined the value of the current at the end of any time within the range employed. For since $\bar{i}=\frac{1}{t}\int_0^t idt$, it follows by differentiation that

$$i_t=\bar{i}+t\left(\frac{d\bar{i}}{dt}\right)_t \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

The simultaneous values of v and R at any moment can thence be calculated. The expression found for the former is

$$v=V\cdot\frac{PS+PQ+G(P+Q)}{PQ+(S+G)(P+Q)}-i\cdot\frac{PQS+GS(P+Q)}{PQ+(G+S)(P+Q)}\cdot \quad . \quad (5)$$

Having thus calculated v, the value of the resistance at the same instant may be found, since

$$R=v/i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It will be observed that the expressions for instantaneous values involve the galvanometer resistance.

It was found that the curves thereby obtained connecting R and v were of the same general trend as those connecting $\frac{P}{Q}\cdot S$ and $\bar{v}\left(=V\cdot\frac{P}{P+Q}\right)$. The latter quantities were, therefore, plotted to represent R and v respectively in the characteristic curves shown in the Paper.

The balance is independent of the inductances in the bridge network, since the initial and final values of all the currents are zero.

Statement of Results of Observation.

Experiments were conducted on zincite, galena, and carborundum ; the other element of the contact being platinum in each case. Two sets of determinations were made, one connecting R and v (τ constant) ; the other connecting R and t (v constant). The results are expressed in the accompanying curves and tables.

Attention was concentrated mainly on zincite, owing to the reliable nature of the contacts which this material furnishes. Many points of contact were tried. Two sets of resistance characteristics, obtained from two of these points, are given in Figs. 2 and 3 ; they include the main features found in all the tests. Parts of the curves are omitted where excessive closeness might cause confusion. It may be seen that—

(1) For current across the contact from zincite to platinum the resistances increases with time, the reverse being true when the current is in the reverse direction. This result holds at all values of the voltage. The changes are more pronounced for the first mentioned direction of current. The curves all pass through the same point at zero voltage.

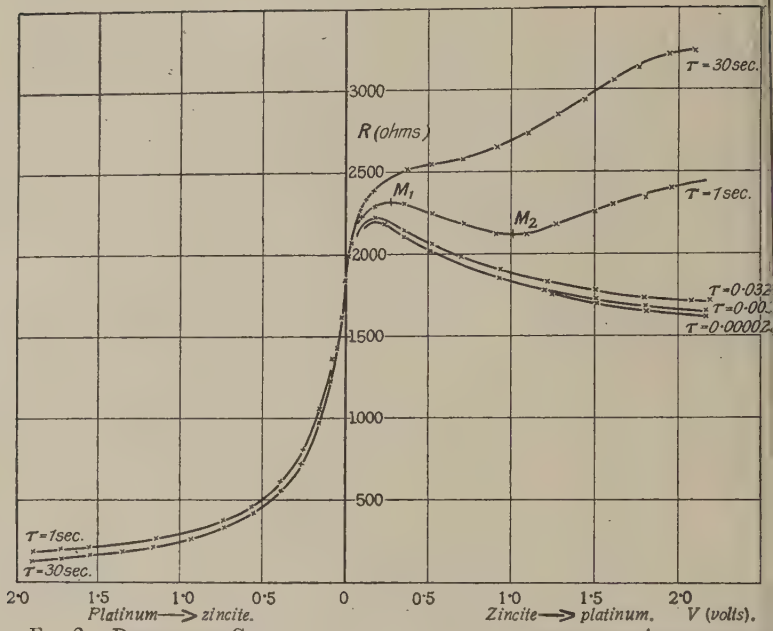


FIG. 2.—RESISTANCE CHARACTERISTICS FOR VARIOUS PERIODS OF APPLICATION OF VOLTAGE. (ZINCITE-PLATINUM.)

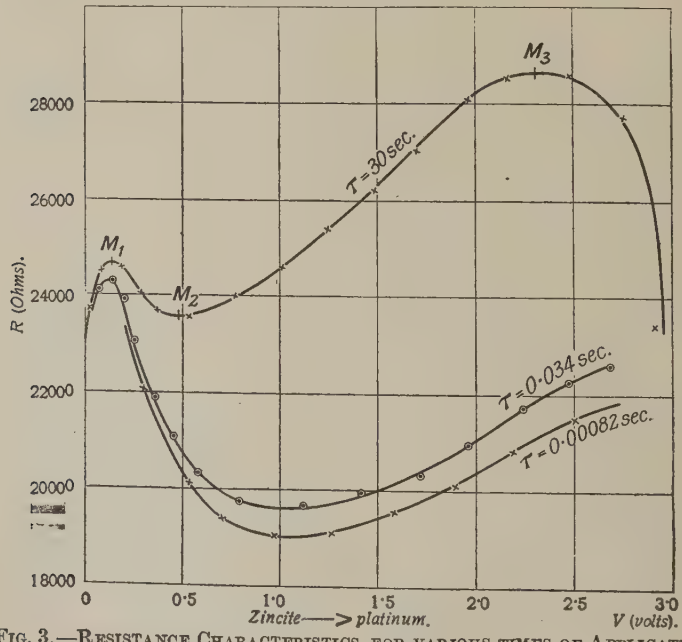


FIG. 3.—RESISTANCE CHARACTERISTICS FOR VARIOUS TIMES OF APPLICATION OF VOLTAGE. (ZINCITE-PLATINUM.)

(2) The effect in the neighbourhood of zero voltage is a slight increase in the slope, or voltage-coefficient, with increase in the time of application of the voltage.

(3) At higher voltages, for current from zincite to platinum (across the contact) the increase of resistance with time may be so great as to produce a minimum point M_2 in the characteristic. This effect is in some cases (*see* Fig. 2) great enough to obliterate the first maximum, which is characteristic of all the curves when τ is small.

(4) When the voltage is increased to a value between 2 and 3 volts, there is a steep fall in the characteristic. At the larger values of τ this is preceded by a second point of maximum, which is more conspicuous for some contacts than for others. (Cf. M_3 in Figs. 2 and 3.)

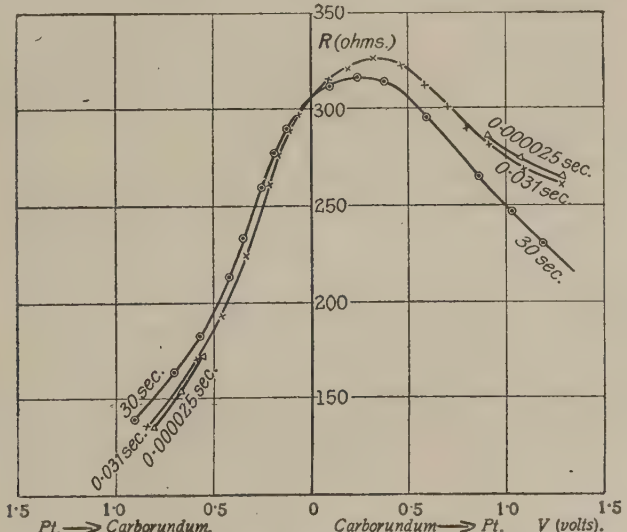


FIG. 4.—RESISTANCE CHARACTERISTICS FOR VARIOUS PERIODS OF APPLICATION OF VOLTAGE. (CARBORUNDUM-PLATINUM.)

Experiments on contacts of *galena* show at low voltages effects of the same kind as those of zincite ; that is, the slope of the characteristic at zero voltage is accentuated by increasing the duration of flow of the current.

In the case of *carborundum* the time effect is contrary in sign to that in the two preceding cases. As shown in Fig. 4, the resistance of a carborundum contact decreases as the current is prolonged, when the direction is from carborundum

to platinum across the contact; the effect being as before reversed when the current is reversed.

The time-effect may be examined from another point of view by determining the resistance of a contact for a series of gradually increasing periods of closure of the battery circuit, the applied voltage being the same in each case. The data shown in Table II. were found in the case of a zincite contact. Applied voltage=2·08 volts; resistance at zero voltage, R_0 =1,311 ohms; voltage coefficient=4·4; current from zincite to platinum across the contact.

TABLE II.—*Variation of Resistance with Duration of Current.*

Time of application of voltage (seconds).	Resistance (ohms.)	dR/dt (ohms/sec.)
0·000025	1,453	140,000
0·00012	1,463	36,400
0·00082	1,477	13,100
0·0031	1,495	4,820
0·032	1,545	1,220
1·0	1,805	163
30·0	2,245	8

The third column shows the rate of change of resistance with time at the end of the period specified in the first column.

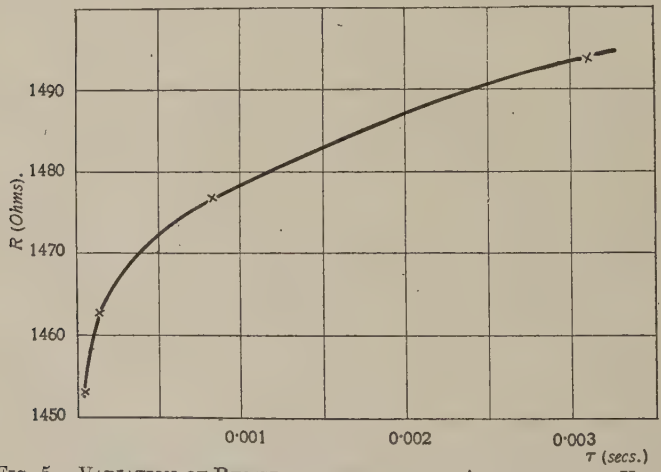


FIG. 5.—VARIATION OF RESISTANCE WITH TIME OF APPLICATION OF VOLTAGE (ZINCITE-PLATINUM CONTACT. R_0=1311 OHMS; v=2·08 VOLTS.)

These observations cannot be represented adequately on a single diagram with one time scale. The curve of Fig. 5 includes the first four points.

As the changes of resistance observed within the range of the part of the curve shown are not great, it may be well to state that great care was taken to avoid errors arising from the variations, steady or erratic, which go on more or less at all contacts when left to themselves. For example, measurements at $\tau=0{\cdot}00082$ second and at $\tau=0{\cdot}00012$ second would alternate with one another until certainty as to the difference of resistance corresponding to these two periods was secured.

From the above table and figure we gather

(5) That the rate of variation of resistance becomes continuously greater as τ becomes less.

Nevertheless, if the time of flow of current be divided into steps increasing in geometrical progression, it is found that, up to a point, the absolute change of resistance in any step becomes greater as we progress along the series. This is shown in Table III., which is deduced from Fig. 5.

TABLE III.

Interval (seconds).	Change of resistance (ohms).
$=0{\cdot}000025$ to $=0{\cdot}00025$	1,467·5—1,453= 14·5
$=0{\cdot}00025$ to $=0{\cdot}0025$	1,492·0—1,467=35·0
$=0{\cdot}0025$ to $=0{\cdot}025$	1,537·0—1,492= 45·0
$=0{\cdot}025$ to $=0{\cdot}25$	1,660·0—1,537=123·0

Interpretation of Results.

The above data enable a judgment to be formed of the relation between the characteristic actually described by a contact under an oscillatory voltage of, say, a million frequency, and that obtained in a slow point by point test.

The time of application of voltage has been varied from 30 seconds to a little under one millionth of that time. A further reduction to one-tenth the lower limit would have yielded a period of the order of 10^{-6} second. The degree of extrapolation involved appears sufficiently small to warrant the conclusion that the characteristic at $\tau=10^{-6}$ second would not materially differ from that obtained at $\tau=0{\cdot}001$ second, or even 0·01 second; though referred to that found at $\tau=1$ second or more the correction required would be very appreciable, especially at the higher voltages.

The sensitiveness of the contact, used as a detector of high-frequency oscillations, and in the absence of a polarising voltage, would in the case of zincite or galena be probably less

by some 10 per cent. or 20 per cent. than that deduced from a long-period characteristic; in the case of carborundum it would be greater by approximately the same percentage.

The bearing of the experimental results on the thermo-electric theory of the contact will now be examined. According to this theory the changes of resistance with voltage are not instantaneous, but are a consequence of the thermo-E.M.F. and the temperature variation of resistance that accompany heat development at the contact. The rate of variation actually observed is very great. To quote one case (*see* Table II.), the resistance of a zincite contact under a voltage of 2·08 volts was 2,245 ohms at the end of 30 seconds; at an instant 0·000025 second after application of the voltage it was 1,453 ohms, the rate of variation then being 140,000 ohms per second. The limiting resistance was 1,311 ohms. It appears not unreasonable to suppose that the outstanding difference of 142 ohms occurred in the first 40,000th of a second; and that the whole difference between the resistance at zero voltage and that found at any other voltage is due to and follows the temperature variation at the contact.

As already pointed out, the characteristic at $\tau=0{\cdot}000025$ second does not very materially differ from that obtained at $\tau=0{\cdot}01$ second, whereas the latter differs considerably from the characteristic at $\tau=1$ second. Again, it appears (*see* Fig. 4) that an initial increase of resistance may be followed by a decrease as the voltage is sustained, or vice versa. These facts point to the necessity of modifying the simple view that the Joulean and the thermo-electric disengagements of heat are located in precisely the same volume of the crystal.

They become intelligible if we suppose two regions of heat development. The question of the location of the resistance at a contact was dealt with (from an altogether different point of view) in the preceding Paper (*loc. cit.*). Two views were discussed. According to the first the resistance may be located within the high-resistance element of the contact, in a volume whose linear dimensions in every direction are of the order of those of the interface $\left(R \doteqdot \frac{0{\cdot}8\rho r_0}{\pi {r_0}^2}\right)$. According to the second view the resistance may be assigned to a stratum of molecular thickness, but of considerable resistance, at the interface of the two elements of the contact.

These views are not mutually exclusive, and the data at

present under discussion give grounds for the conclusion that the resistance is made up of the two in series, as illustrated in the diagram of Fig. 6.

The Peltier heat would be developed solely in the second region. Joulean heat would be set free in both regions, as also would the Thomson heat. Joulean heat is always positive. The Thomson heat, like the Peltier heat, may be either positive or negative ; but in contrast to the Peltier heating effect, its sign is (for small currents) unaffected by the direction of the current.

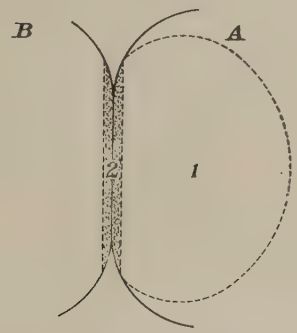


FIG. 6.—DIAGRAM ILLUSTRATING VIEW OF TWO REGIONS OF HEAT DEVELOPMENT AT A CONTACT.

A represents the high-resistance element ; *B* the low-resistance element of the pair. Region 1 has linear dimensions of the order of those of the interface ; region 2 is a stratum of molecular thickness

Extremely rapid change of temperature is regarded as associated with heat liberated (or absorbed) in region 2 ; and slow change with thermal effects occurring in region 1. There are thus two " time-constants," one, proper to the molecular stratum, being very small compared with the other.

The Thomson heat may possibly account for the difference in the two types of crystal, one represented by zincite, the other by carborundum (*see* Figs. 2 and 4). If the thermo-E.M.F. be represented by a parabolic formula (the experiments of Bidwell* appear to point to this law for oxides, sulphides, &c.), then writing

$$e=a(T-T_0)+c(T^2-T_0^2) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in place of the simple linear formula used in the previous Paper,

* " Phys. Rev.," 1914.

we find for the slope of the characteristic at zero voltage the modified expression

$$\left(\frac{dR}{dv}\right)_0=\frac{-R_0\frac{P_0}{T_0}\left(1+bT_0+\frac{cP_0T_0}{KR_0}\right)}{KR_0}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in which P_0=Peltier coefficient at the absolute temperature T_0 of the surroundings; b=temperature coefficient of resistance; K=dissipation constant.

If the Thomson heat develops slowly, then the question of increase or decrease with time of the slope at zero voltage will be determined by the sign of the coefficient c. A zincite contact behaves as if c were negative; a carborundum contact as if c were positive.

A Thomson absorption of heat (accompanied by a negative temperature-coefficient of resistance) appears also a probable cause of the rise of resistance up to the second maximum (*see* Fig. 3) which occurs when the current is sustained for a comparatively long period.

The characteristic obtained at a zincite contact when the voltage is sustained for a considerable period is conspicuous by the presence of a second maximum. The curve rapidly descends past this point, and once this has been permitted to happen the limiting resistance of the contact is found to be only a small fraction of the initial value. This drop, which is permanent, is to be assigned to softening due to rise of temperature; this leading in its turn to increase of area and consequent reduction in electric resistance. The effect here outlined is doubtless to be identified with the "breakdown" found in practice when a contact has been subjected to an excessive voltage.

The Values of the Time Constants.—Accepting thermoelectric action as the true basis of the rectifying property, a time lag of resistance must inevitably occur; but this, if it is not to nullify the rectifying action, must be of comparatively small account even at the rapidity of change involved at electric wave frequencies. This can only be the case if an appreciable portion of the resistance of the contact is associated with a time-constant small compared with the period of the impressed oscillations.

It is possible to form estimates of the time-constants corresponding to the regions 1 and 2 of Fig. 6; the dimensions of the contact, the thermal conductivity and the specific heat of

the material entering as important factors. The heat dissipation may be attributed entirely to conduction to neighbouring portions of the crystal—this restriction will tend to yield a maximum estimate. Two problems may first be considered in the abstract.

Problem I.—Suppose heat to be developed at a constant rate within a small sphere in the interior of an infinite uniform solid mass. For simplicity assume the temperature to be constant at any instant at all points within the sphere. What is the time-constant which defines the rate of rise of temperature of the boundary of the sphere?

Let θ_0 denote the initial temperature, θ the final temperature of the sphere, k the thermal conductivity, d the density, s the specific heat, H the rate of supply of heat, r_0 the radius of the sphere, and T the time-constant required.
It is easy to show that

$$\theta-\theta_0=\frac{H}{4\pi k r_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The temperature change occurring in accordance with a simple exponential law, we have

$$T=\frac{\theta-\theta_0}{(d\theta/dt)_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Also $$\left(\frac{d\theta}{dt}\right)_0=\frac{\text{rate of supply of heat}}{\text{thermal capacity of sphere}}=\frac{H}{\frac{4}{3}\pi r_0^3 ds}. \quad . \quad (11)$$

Combining the above equations,

$$T=\frac{r_0^2 ds}{3k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Now in the case of zincite, &c., we may take $ds \doteqdot 0{\cdot}5$, and $k \doteqdot 0{\cdot}005$, whence

$$T \doteqdot 33 r_0^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Hence, if $T < 10^{-7}$ second, then $r_0 < 0{\cdot}5 \times 10^{-4}$ cm.

The second problem is intended to relate to a stratum of molecular thickness, such as a circular disc, enclosed within an infinite solid. The difficulty of dealing with the edge effect may be avoided without materially affecting the calculation if we substitute a spherical shell of the same area. We may then state the problem thus :—

Problem II.—Suppose a spherical shell of molecular thickness forming the boundary of a spherical hollow in the interior of an infinite solid ; and that within the material of the shell heat is

developed at a constant rate. Assuming equality of temperature within the shell at any instant, what is the value of its thermal time-constant?

Using the same symbols as before, we have

$$\theta - \theta_0 = \frac{H}{4\pi k r_0}, \quad \ldots \ldots \quad (14)$$

and $$\frac{\theta - \theta_0}{T} = \frac{\text{rate of supply of heat}}{\text{thermal capacity of shell}} = \frac{H}{4\pi r_0^2 ds \,.\, 10^{-8}}, \quad (15)$$

whence $$T = \frac{r_0 ds}{k} \,.\, 10^{-8} \quad \ldots \ldots \quad (16)$$

Taking $ds \doteqdot 0{\cdot}5$, $k \doteqdot 0{\cdot}005$, we find $T \doteqdot r_0 \,.\, 10^{-6}$ second. Hence if $T < 10^{-7}$ second, then $r_0 < 0{\cdot}1$ cm.

We may identify the conditions of the above problems with those occurring in regions 1 and 2 respectively of a rectifying contact. The assumption of infinite conductivity within the small sphere and in the stratum has the effect of reducing the value of T calculated, and hence of increasing the value fo r_0 corresponding to a selected value of T. The attendant error only enhances the deductions drawn, namely, that the variations of temperature and resistance at a contact can only follow the voltage without serious diminution at electric wave frequency—

(*a*) In region 1 if the mean diameter of the area of contact $< 0{\cdot}5 \times 10^{-4}$ cm.;

(*b*) In region 2 if the mean diameter $< 0{\cdot}1$ cm.

Now in actual practice the mean diameter of the area of a good rectifying contact is as a rule far greater than 10^{-4} cm. The conclusion is that the only variation in resistance that can be effective in causing rectification at very high frequency must have its origin in a stratum of molecular thickness at the actual interface of the contact. What the composition of the stratum is there are not at present sufficient data to determine. It is required of it that it should be very thin—indeed of molecular thickness; that it should have a resistivity far higher than that of the material of the contact treated in bulk; and that it should have a negative temperature-coefficient of resistance.

This conclusion accords both with the experimental results and with the calculated maximum rate at which it is possible for a defined volume of material to vary in temperature when subjected to a constant source of heat. That the rate of supply of electrical energy which is found to operate the receiving circuit of a wireless station is adequate to produce the required

thermal effects at the rectifying contact may be shown by simple calculation.

Summary.

The resistance at a solid rectifying contact, and consequently the exact shape of the resistance characteristic, depends upon the time for which the testing current is allowed to flow. A series of characteristics are given corresponding to durations of contact extending over the range one forty-thousandth of a second to 30 seconds.

The following conclusions are drawn :—

1. That the variation of resistance with voltage may be attributed entirely to thermal effects.

2. That the characteristic obtained by applying the testing voltage for one hundredth of a second is, at moderate voltages, materially the same as that which would be found at the expiry of a period of the order of a millionth of a second.

3. That the sensibility of a wireless receiving circuit (in which the rectifying contact is used) does not differ very appreciably from that deduced from a slow period characteristic.

4. That an important fraction of the contact-resistance resides in a stratum of molecular thickness at the interface of the two elements of the contact ; and that it is in this region alone that rectifying action at very high frequencies is effected.

DISCUSSION.

Prof. G. W. O. Howe thought the experimental method of Mr. Owen was the correct way to tackle the problem of high frequency phenomena, and was preferable to taking oscillograph records at low commercial frequencies, and attempting to deduce from them what will happen at very much higher frequencies. What is the limit to the number of times per second that the ball may be struck for the results still to apply to one impact only ? From one point of view the results were disappointing, inasmuch as it had been necessary to introduce a mysterious stratum of molecular thickness and the problem arises as to what these layers consist of ; what are their properties, and why is the thermal effect largely confined to them ?

Dr. H. S. Allen asked if any attempt had been made to remove surface films from the contacts. Prof. Millikan had recently obtained very simple results in photo-electricity by working in a high vacuum, so as to remove all films of moisture. Could this not be done in Mr. Owen's experiments ?

Dr. Eccles said that the subject of contact resistance was of wide importance, apart from its application to electric wave detectors. It had been investigated by Wheatstone and Heaviside in other connections—microphones, for example. It was important also in connection with the contacts at dynamo brushes. There had always been a desire in wireless telegraphy circles for high-frequency characteristic curves. Doubtless, if oscillograph records could be obtained for frequencies of 10^{-6} second, they would be very like what Mr. Owen gets by his point to point method. He would have been glad if the author had tried similar contacts—*e.g.*, two carbons, two galenas, or even two metals. In these cases there would be no thermo-electric phenomena to confuse the issue. He was not con-

vinced on the question of the molecular layer. The author states that "in actual practice the mean diameter of the area of a good rectifying contact is, as a rule, far greater than 10^{-4} cm." Now, if one pictures a piece of metal resting on the zigzag surface of a crystal, it is obvious that actual contact will only occur at points and ridges, and it is surely impossible for anyone to assert what the order of the area of contact is. He preferred to think that the effects were due to the heating of the surface layers of the stuff, due to concentration of the current flow into the narrow regions where actual contact exists. Usually, the harder the crystal the better the rectification obtained, due possibly to the greater concentration of current in the smaller and sharper contact points. He thought perhaps too much stress was laid on the high-frequency characteristic. When an oscillation passes through the contact of a crystal touching a metal plate it is the after effects of the heat developed which produce the thermo-electric currents that affect the telephone. Therefore, while of scientific interest, the high-frequency characteristics are not very essential from the point of view of wireless telegraphy.

Mr. F. E. Smith thought Dr. Allen's suggestion a valuable one. About 14 years ago a Paper was read to the Society showing that films of liquid remained attached to solids even up to temperatures of 300°C.

The Author, in reply to Prof. Howe, thought there was no mystery in the contact layer. We cannot assume complete continuity of material at a contact as in a weld. This is evidenced by the fact that no appreciable force is required to separate the elements, though they have been pressed together with a force involving a considerable minimum area of contact. With respect to the repeated impacts (used in order to raise the sensibility of the bridge), the time between the successive impacts was never less than about 8,000 times the duration of a single contact. The point raised by Dr. Allen, and emphasised by the chairman, deserved investigation. Dr. Eccles raises two important points. In order to avoid the necessity of assuming a molecular stratum, he suggests the view of multiple contacts. This, if carried out to the requisite minute subdivision of the total contact area, will certainly effect the required reduction of the thermal time-constant. I have taken the opportunity of submitting the matter to calculation. I find that the time-constant will be reduced to 10^{-7} sec., provided the number of effective contacts, all of equal area, is not less than 25,000, and this number must, on grounds of probability, be regarded as only a small proportion of the total number of contacts under the total area, on the view under discussion. It seems a case of choosing between a molecular layer and an ark resting on a hundred thousand Ararats, the size of each peaklet not far removed from molecular dimensions. Dr. Eccles also asserts the view that the electric discharge which actuates the telephone in a wireless receiving circuit is due to the *after effect* of the heat accumulated at the contact; but this is to neglect altogether the rectified current that traverses the contact during the actual period of impress of the electric oscillations, and this is amenable to calculation (*see* Paper in Vol. XXVIII., p. 196). I find that the impulsive flow due to the rectified current would be sufficient to produce an audible effect in the telephone provided the mean amplitude of the wave of P.D. across the contact during the passage of a train of oscillations is somewhere between one hundredth and one-tenth of a volt. Now at such low voltages the reversible Peltier heat (on which rectification depends) in the case of crystals like zincite exceeds the irreversible Joulean heat (on which the after effect depends). Curious as it may at first sight appear, the power expended in the alternate Peltier heating and cooling greatly exceeds, at low voltages, the total electrical power supplied to the rectifying sector by the incident oscillations. There is thus reason for regarding the signal in the telephone as due mainly to the rectified current. In reference to phenomena at a contact between similar materials, I have at present under consideration the investigation of the effect of pressure at such contacts.

III.—*On Diffusion in Liquids.* *By* Basil W. Clack, *M.Sc. (Lond.), Lecturer in Physics at Birkbeck College.*

Received September 28, 1916.

§ 1. *Introduction.*

It has recently been pointed out by Griffiths ["A Recalculation of some Work on Diffusion," Proc. Phys. Soc., Lond., XXVIII., p. 255, 1916] that a correction is necessary to the theory of the method which has been used by the author for studying the diffusion of salts through water. [*See* Clack: (1) "On the Coefficient of Diffusion," Proc. Phys. Soc., XXI., p. 863, 1908; (2) "On the Temperature Coefficient of Diffusion," Proc. Phys. Soc., XXIV., p. 40, 1911; (3) "On the Coefficient of Diffusion in Dilute Solutions," Proc. Phys. Soc., XXVII., p. 56, 1914.] In these Papers experiments are described in which diffusion has been studied by means of special flasks, filled with the solution under investigation, and suspended in a large bath of water at known constant temperatures. The design of the flasks is such as to maintain the concentration of the solution constant at each end of the vertical tubes which are fitted into the flask, so that diffusion takes place in the steady state, that is to say, the concentration of the solution at any point in the tube remains constant while the measurements are made.

The decrease in volume of the solution in the flask as diffusion reduces its concentration, causes a current of liquid to flow down the tube, so that as the salt diffuses upwards it meets a current of liquid which continually passes downwards, and which is due to the decrease in volume referred to. In the Papers mentioned above, reference was made to the velocity of this current of solution; but the matter is complicated by the fact that simultaneously with the movement of the water in the solution the dissolved salt is diffusing, and therefore may have quite another velocity, and on this account it is necessary to confine attention to the velocity of the water component of the solution.

§ 2. *Objects.*

The objects with which this communication is made, are two:—

1. To amend the theory in the direction indicated; to present the recalculated values of the coefficient of diffusion at different temperatures and at various concentrations; and to

evaluate the temperature-coefficient of diffusion in the case of certain solutions.

2. To deduce an expression for the coefficient of diffusion, K_n, at any definite concentration, n, which is now rendered possible by the simpler form of the corrected formulæ deduced in the next section; and to find the numerical value of this quantity for specified concentrations of solutions of certain salts.

§ 3. *Theory.*

The theory previously published in the first Paper mentioned in § 1 must be amended as follows :—

Let L = total length of the diffusion tube.

N = constant concentration of solution at bottom of the diffusion tube in gms./cc.

D = its constant density.

n = concentration of the solution at a point l cms. below the top of the tube when the steady state has been reached.

d = density of the solution at the same point.

v = velocity downwards of the water-component of the solution in the tube at the same point.

v_0 = velocity downwards of the water at the top of the the tube, where $l=0$.

Assume the area of cross-section of the tube is unity. Now 1 cc. of solution contains $(d-n)$ grammes of water, and since the same mass of water crosses each section of the tube per second in the steady state

$$v(d-n)=v_0.$$

Also, when the steady state is reached, the mass of salt passing each section of the tube per second is constant$=c$.

The change, i, in weight of the flask per second is equal to the mass of salt leaving it per second minus the mass of water entering per second, or in symbols

$$i=c-v_0.$$

Let δ represent the ratio of the change in volume produced in the solution, to the change in the amount of salt present. Then, since every second c grammes of salt escape from the flask, the volume changes by $c\delta$ cc., or $c\delta$ cc. of water enter the flask per second from the bath,

i.e., $$v_0=c\delta.$$

Thus $v=c\delta/(d-n)$

and $i=c-c\delta$

$=c(1-\delta)$.

In the previous work the mistake was made of assuming that $c\delta$ cc. of *solution* entered the flask from the tube. The error will be made quite obvious if the upper end of the tube is considered, instead of the lower; or it can be argued that if c grammes of salt leave the flask, the volume they occupied must be taken by *water*, and not by solution, for if so, some salt would return into the flask and the quantity leaving would not be c.

Under the combined actions of the movements of the liquid and diffusion it follows that

$$c=-vn+Kdn/dl.$$

Substituting the value of v already found

$$c(d-n+n\delta)/(d-n)=Kdn/dl \quad . \quad . \quad . \quad . \quad (1)$$

Now d is approximately a linear function of n and we make very little error if we assume that over any given range of concentration $d=1+an$, where a is some constant depending slightly on the upper limit of concentration N, and whose value may be considered to be very approximately equal to the mean slope of the true curve of d and n between the limits zero and N.

If b is written for $(1-a)$ equation (1) becomes

$$\{c+n(v_0-bc)\}/(1-bn)=Kdn/dl,$$

the solution to which is

$$-\frac{bN}{v_0-bc}+\frac{v_0}{(v_0-bc)^2}\log_e\frac{(v_0-bc)N+c}{c}=\frac{L}{K}. \quad . \quad . \quad (2)$$

Since $(v_0-bc)N$ is small compared with c this may be written

$$\frac{N}{c}\left[1-\frac{v_0N}{2c}+\frac{v_0(v_0-bc)N^2}{3c^2}\ldots\right]=\frac{L}{K}. \quad . \quad . \quad (3)$$

These equations are exactly of the same form as those already published in equations (2) and (3), Proc. Phys. Soc., XXI., p. 865, 1908, where it was mentioned that the third term in the bracket in equation (3) was negligible. Owing to the correction now introduced this term is still smaller, and hence we may write

$$\frac{N}{c}\left[1-\frac{v_0N}{2c}\right]=\frac{L}{K},$$

or since $v_0=c\delta$

$$c=\frac{KN}{L}(1-\tfrac{1}{2}N\delta), \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

i.e., as $c=i/(1-\delta)$

$$K=\frac{Li}{N(1-\tfrac{1}{2}N\delta)(1-\delta)}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It is interesting to note that this equation does not involve any knowledge of a or b or D. δ is readily obtained from the published Tables connecting density and concentration.

Thus the equations on p. 866 in the first Paper mentioned in § 1 must be corrected by omitting in every case the factor $(1-bN)$. In the second and third Papers the corresponding factor $(D-N)$ must be deleted, so that the value of K is obtained from the equation

$$K=\frac{L_1L_2}{A_1L_2-A_2L_1}\times\frac{i_1-i_2}{N(1-\tfrac{1}{2}N\delta)(1-\delta)}.$$

§ 4. *The Coefficient of Diffusion at Different Temperatures.*

The following table gives the results for solutions of potassium chloride and nitrate at the concentrations and temperatures mentioned. In the first column the figure 1, 2 or 3 indicates the Paper in which the result was previously published (*see* § 1), while the second column gives the number of the experiment, in order that comparison can be made and the magnitude of the correction estimated.

20 per cent. KCl or 2·7 normal or $N=0\cdot2$ gm./cc.

Paper.	Experiment.	Temp. in °C.	$K\times10^5$ C.G.S.
1	24	0	1·040
1	25	0	1·054
2	4	0	1·042
2	5	13	1·391
2	6	14	1·408
3	28	18·8	1·633
3	10	18·7	1·663
3	11	18·8	1·666
2	12	23·7	1·766
2	13	23·8	1·760

10 per cent. KCl or 1·34 normal or $N=0·1$ gm./cc.

1	26	0	0·987
1	27	0	0·989
2	7	14·6	1·412
2	8	15·8	1·479
2	9	16·9	1·507
3	8	18·6	1·545
3	9	18·7	1·545
2	14	23·8	1·785
2	15	23·9	1·782

10 per cent. KNO_3 or 1·0 normal or $N=0·1$ gm./cc.

Paper.	Experiment.	Temp. in °C.	$K\times10^5$ C.G.S.
1	16	0	0·873
1	17	0	0·875
2	10	15·1	1·266
2	18	16·3	1·292
3	30	18·9	1·338
3	31	19·0	1·358
2	16	23·4	1·519
2	17	23·6	1·520

5 per cent. KNO_3 or 0·5 normal or $N=0·05$ gm./cc.

1	22	0	0·885
1	23	0	0·887
2	19	16·2	1·286
2	20	16·3	1·303
3	42	18·3	1·371
3	32	19·1	1·445
3	33	19·2	1·421
2	21	25·0	1·547
2	22	25·6	1·575

A comparison of these figures with those previously published shows that the correction causes an increase in the numerical value obtained for the diffusivity which amounts to 6 or 7 per cent. in the case of 20 per cent. solutions of potassium chloride. For a similar solution of sodium chloride the correction is found to be only 4 per cent. In less concentrated solutions the

correction is smaller, being roughly proportional to the concentration, and may be considered to be within the probable error of observation for all solutions weaker than 10 per cent.

§ 5. *The Temperature Coefficient.*

From the above figures the corrected values of the temperature coefficient can be calculated.

Thus if $K_t = K_0 (1 + at + bt^2)$ the values of a and b are as follows, for the four solutions mentioned :—

Salt.	Normality.	N in gm./cc.	$K_0 \times 10^5$	a	b
KCl	2·7	0·2	1·045	0·020	0·00050
	1·35	0·1	0·988	0·023	0·00047
KNO_3	1·0	0·1	0·874	0·023	0·00032
	0·5	0·05	0·886	0·024	0·00027

These figures indicate that in the neighbourhood of 18°C. the simpler formula approximately holds

$$K_t = K_{18}\{1 + a(t-18)\},$$

where a has the value 0·024 for all these solutions.

For 2·7 normal KCl at 18°C. we find

$$K_{18} = 1{\cdot}639 \times 10^{-5} \text{ sq. cm./sec.}$$

Dr. Griffiths by two different and independent methods obtains for a similar concentration and temperature the values $1{\cdot}696$ and $1{\cdot}617 \times 10^{-5}$ respectively. [*See* Griffiths, Proc. Phys. Soc., XXVIII., p. 255, 1916.]

§ 6. *The Coefficient of Diffusion at Different Concentrations.*

If the temperature be maintained constant during each experiment, and in the neighbourhood of 18·5°C. we obtain in the same way recalculated results for solutions of potassium chloride, potassium nitrate and sodium chloride, which are plotted graphically in Fig. 1, and, in order to save space, the values, obtained from the graphs, of the diffusivity at 18·5°C. for solutions of the concentrations indicated in the first column, are tabulated on next page.

Normality.	KCl $K \times 10^5$	KNO_3 $K \times 10^5$	NaCl $K \times 10^5$
0·05	1·364	1·502	1·159
0·1	1·412	1·475	1·163
0·2	1·446	1·446	1·169
0·4	1·475	1·409	1·181
0·6	1·491	1·382	1·190
0·8	1·506	1·362	1·201
1·0	1·521	1·344	1·209
1·5	1·558	...	1·226
2·0	1·598	...	1·240
2·5	1·636	...	1·255
3·0	...	...	1·268

§ 7. *Diffusion at a Definite Concentration.*

In practically all the methods of determining the diffusivity of salts previous to those employed by the author and his colleagues, no attempt is made to use the steady state of diffusion. That is to say, the rate of diffusion is studied before it becomes constant, and the concentration at any point in the solution is continually changing while the experiment is in progress. As is well known, the coefficient of diffusion is not the perfectly constant quantity which Fick's law indicates; but it varies, in some cases considerably, with the concentration of the solution, so that it appears impossible in the present state of development of the theory of diffusion to say to what concentration the coefficient obtained refers.

The interpretation is less indefinite if the steady state is employed in which the concentration at each point of the solution remains quite constant while the measurements are made. These measurements give what the author has called the "mean diffusivity," K, for the solution in the diffusion tube, that is, for a solution varying in concentration from zero to a certain maximum, N, in each experiment, and from the determination of this quantity it is found possible to calculate the value of the actual diffusivity, K_n, for a solution of a definite concentration, n, in the following manner :—

The equation for c (equation (4) above) might have been obtained by making the initial assumption in equation (1) that $\delta = b$. This assumption is not strictly true, but even in the strongest solutions it only introduces a small error—probably of the order one-fifth of 1 per cent.—in the value obtained for the coefficient of diffusion, and this error is smaller the more dilute the solution.

With this approximation equation (1) becomes

$$K_n=\frac{c}{1-n\delta}\frac{dl}{dn}.$$

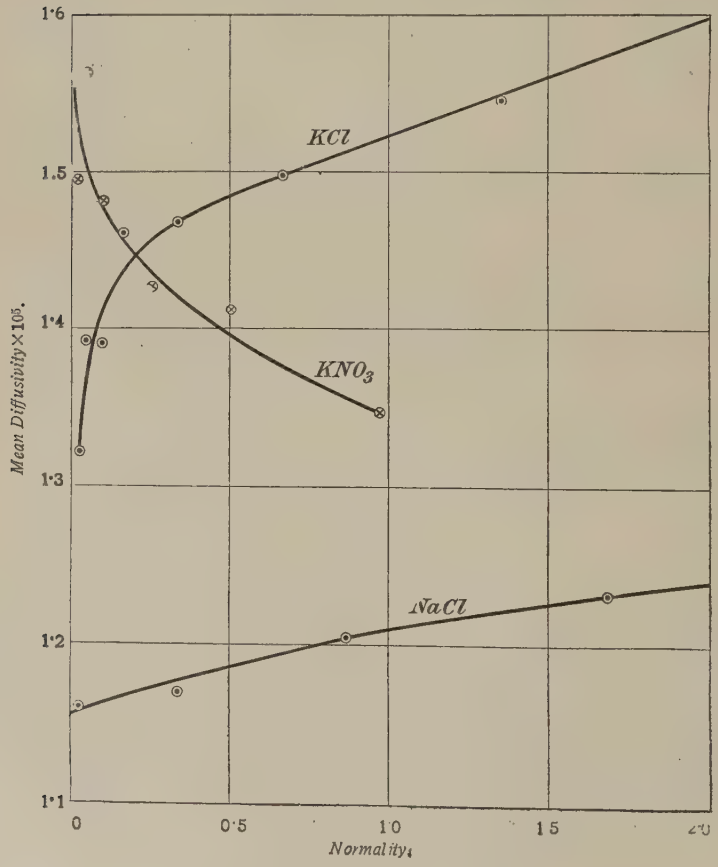
By integration this gives

$$K\times n(1-\tfrac{1}{2}n\delta)=cl,$$

where K will represent the mean diffusivity over the range of concentration 0 to n.

Differentiating this with respect to n and noting that c is a constant in any given experiment, we have

$$K+\{(1-\tfrac{1}{2}n\delta)/(1-n\delta)\}n\,.\,dK/dn=\frac{c}{1-n\delta}\frac{dl}{dn}=K_n. \quad . \quad (6)$$



So that we can find the value of the coefficient, K_n, at any definite concentration, n, from the above expression involving a measurement of the slope of the experimental curves shown in Fig. 1.

The values of the coefficient of diffusion at 18·5°C. in C.G.S. units (sq. cm./sec.) thus obtained at the definite concentrations indicated in the first column are tabulated below :—

Normality.	KCl. $K_n \times 10^5$	KNO_3 $K_n \times 10^5$	NaCl. $K_n \times 10^5$
0·05	1·442	1·464	1·164
0·1	1·459	1·435	1·170
0·2	1·488	1·402	1·181
0·4	1·511	1·349	1·202
0·6	1·534	1·315	1·220
0·8	1·564	1·285	1·238
1·0	1·598	1·259	1·248
1·5	1·675	...	1·273
2·0	1·755	...	1·397
2·5	1·834	...	1·327
3·0	...	...	1·355

In a previous Paper (Proc. Phys. Soc., XXVII., p. 64, 1914) the author attempted to obtain this quantity K_n but was obliged to make certain assumptions as to the movement of the liquid which were not strictly in accordance with the facts, owing to mathematical difficulties in the treatment of the real conditions obtaining in the experimental work, but the simpler formulæ now found to be correct enable the actual diffusivity at any definite concentration to be evaluated for the first time without making the assumptions just referred to. As has already been mentioned, this calculation appears to be impossible unless the steady state is employed, and represents a new departure in work on diffusion.

ABSTRACT.

The Paper contains the results of the experiments described by the author in Proc. Phys. Soc. Lond., XXI., p. 374, 1908 ; XXIV., p. 40, 1911 ; and XXVII., p. 56, 1914, collected and recalculated in accordance with a theoretical correction recently communicated by Dr. Griffiths (Proc. Phys. Soc., XXVIII., p. 255, 1916).

It is found that in the solutions employed the correction is not considerable, except in the case of the strongest solutions of KCl (2·7 normal), where it amounts to 6 per cent.

The Paper contains the corrected theory of the method, and the value of the coefficient of diffusion is tabulated at different limiting

concentrations and at various temperatures; it concludes with a new method of calculating the coefficient at a definite concentration from the experimental results, which appears to be more accurate and free from questionable assumptions than previous calculations of a similar nature.

DISCUSSION.

Prof. G. W. O. Howe asked why the concentration was constant at the bottom of the diffusion tube in the author's apparatus.

Prof. Boys thought this was an important point. He presumed that the upper bulb was sufficiently large that for the purposes of the experiment it could be regarded as an infinite reservoir. A steady state would then be maintained by the circulation through the side tubes, dilute solution rising up one into the reservoir, while more concentrated solution passed down the other.

Dr. R. S. Willows asked why the coefficient of diffusion was greater for strong than for weak solutions in the case of some salts, while the reverse was true for other salts.

Mr. Clack, in reply to Dr. Willows, said he did not know of any reason, but Dr. S. W. J. Smith had told him that that was what would be expected from conductivity data.

IV.—*On the Measurement of the Thomson Effect in Wires.* By H. Redmayne Nettleton, *M.Sc., Assistant Lecturer in Physics at Birkbeck College.*

Received October 25, 1916.

I. Introduction.

The object of this research is to develop a method of measuring the Thomson Effect in wires for which also the thermo-electric powers may at the same time be found.

It is well known that the application of thermodynamics to thermocouples leads to the two standard equations :—

$$\Pi = T \cdot \frac{dE}{dT}, \quad \ldots \ldots \quad (1)$$

where Π is the Peltier coefficient at the absolute temperature T and dE/dT the thermo-electric power ; and

$$\sigma_a - \sigma_b = -T \cdot \frac{d^2E}{dT^2}, \quad \ldots \ldots \quad (2)$$

where σ_a and σ_b are the respective Thomson effects in the metals comprising the thermocouple.

Equation (1) was first investigated experimentally by Campbell[1] and a little later verified by Jahn[2] with the ice-calorimeter, and since the further development of the measurement of the Peltier effect by Lecher,[3] Cermack,[4] Barker,[5] Oosterhuis,[6] and Callendar[7] it may be said that this equation has been substantiated beyond all doubt. Szarvassi,[8] indeed, regards this equation as the fundamental formula of thermo-electric phenomena and Callendar uses it for his values of Π in measuring heat by the radio-balance.

Equation (2), however, has never been verified. On the contrary, the best measurements of the Thomson effect seem to throw great doubt on the equation (Szarvassi), and so grave is this divergence in the case of the iron-mercury thermocouple

[1] Campbell, " Proc. Roy. Soc. Edin.", p. 387, 1887.
[2] H. Jahn, " Wied. Ann." 34, 755, 1888.
[3] E. Lecher, " Wien. Ber." II.A., 115, p. 1505, 1906.
[4] P. Cermack, " Wien. Ber." II.A, 116, pp. 657 and 1135, 1907.
[5] Barker, " Phys. Rev." XXXI. (4), 321, 1910.
[6] Oosterhuis, " Arch. Néer " Ser III A II, 1912.
[7] Callendar, " Proc. Phys. Soc. Lond." 23. I., Dec., 1910.
[8] Szarvassi, " Ann. der Phys." 17, 248, 1905.

treated of by Schoute,[1] Aalderink[2] and Oosterhuis[3] that the last-named experimenter raises the whole question of the energy of a thermo-electric circuit and states that the Peltier and Thomson effects together do not nearly suffice to supply the energy of the thermo-electric current.

Before, however, any general conclusions can be made on this matter a vast amount of experimental research on the Thomson effect is needed, for it must be remembered that not only is the measurement of the Thomson coefficient one of considerable difficulty, and that impurities have a very great effect, but that many of the methods employed—especially the older ones—are open to severe criticism, particularly when viewed in the light of Verdet's[4] differential equation. As an illustration of what equation (2) leads to we have the following: The thermocouple iron-german silver between 0°C.—200°C. gives a curve for thermo-electric force and temperature which is remarkably linear (Campbell[5], Stewart[6]); iron-nickel and iron-constantan behave somewhat similarly. Hence over this temperature range d^2E/dT^2 is nearly zero and the Thomson effects in iron, german silver, nickel and constantan should approach equality. Now, in a very careful research, Aalderink[7] has shown that the value of σ in iron changes sign at 95°C. and is given by

$$\sigma=(95-t)\times 4{\cdot}9\times 10^{-8} \text{ cal. per coulomb.}$$

Do, then, these other metals show any similar remarkable change of sign or equality of value?

It was thus the author's first intention to measure the Thomson effect in wires of the high-resistance alloys and at the same time measure their thermo-electric powers when combined in pairs. As, however, the Thomson effect is not known with any certainty even in metals like bismuth and platinum in which it is largest, and as the method here described has proved rapid and sensitive, it is now proposed to measure the effect in as many metals as possible. In the present communication it is proposed to deal only with the method itself, investigating the errors, sensibility, and best conditions of experiment.

[1] Schoute, "Arch. Néer." (2), 12, 175, 1907.
[2] Aalderink, "Arch. Néer." (2), 15, 321, 1901.
[3] Oosterhuis, *loc. cit.*
[4] Verdet, "Theorie Méchanique de la Chaleur."
[5] Campbell, "Proc. Roy. Soc. Edin.," 1882.
[6] Stewart, "Phil. Trans." A., p. 569, 1893.
[7] Aalderink, *loc. cit.*

2. The Proposed Method and Its Relation to Other Methods.

The many methods which have been employed to measure the Thomson effect may be classified under four headings :—

(*a*) Battelli's method[1] in which σ is measured directly by the rate of rise of temperature of a calorimeter of known total water equivalent.

(*b*) Haga's method,[2] of which there are many modifications, in which the effect of Thomson heat is compared with the effect of a known amount of Joulean heat.

(*c*) Callendar's method,[3] carried out by King, in which σ is deduced from the variation of resistance with temperature of the wire under test.

(*d*) The impressed velocity method of the author,[4] in which the Thomson effect is neutralised or compared with the effect of a slow uniform movement of the conductor.

Battelli's method is chiefly of historic interest, though there is no doubt it might be modernised ; not only were his experiments complicated by working during the variable state ; but a study of the distribution of temperature down the bar leads to the conclusion that much of the Thomson heat produced outside the calorimeter contributes by conductivity to its rise of temperature. This method which is criticised by Callendar[5] and King for other reasons also lacks sensibility.

Method (*d*) is suitable only for fluids.

Method (*c*) alone has been applied to a wire ; it is of great interest though complicated by the insertion of potential leads. By its nature it is unsuited to the alloys of small temperature coefficient.

Method (*b*), Haga's method, is by far the most generally employed, and undoubtedly of the greatest importance, modifications of it being used by such recent experimenters as Laws,[6] Lecher,[7] Schoute,[8] Berg,[9] and Aalderink.[10] When employing this method it must always be remembered that

[1] Battelli, " Accad. delle Sci. di. Torino," Atti XXII., p. 548, 1887.
[2] Haga, " Ann. de l'ecole Polyt de Delft," I., p. 145, 1885 ; III., p. 43, 1886.
[3] King, " Amer. Acad. Proc." XXXIII., p. 353, 1898.
[4] Nettleton, " Proc. Phys. Soc. Lond.," Dec., 1912.
[5] Callendar, " Encyclo. Brit." Thermo-electricity.
[6] Laws, " Phil. Mag." VII., p. 560, 1904.
[7] Lecher, " Ann. de Physik." XIX., p. 853, 1906.
[8] Schoute, *loc. cit.*
[9] Berg, " Ann. de Physik." XXXII.-XXXIII., p. 477, 1910.
[10] Aalderink, *loc. cit.*

Thomson heat and increments of Joulean heat are only propagated similarly when small and of the same order of magnitude, and that close attention must be paid to the emissivity conditions.

In perhaps its most modern general form Haga's method is produced as follows : A current of C amperes is passed down a bar in which a temperature gradient is maintained. This current is reversed and the ultimate change of temperature $\Delta\theta_T$ is recorded as shown by a thermocouple in the middle of the gradient. The current is then raised or diminished by an amount c amperes, and the difference of temperature $\Delta\theta_J$ is observed between the average temperature given by $+C$ and the average temperature given by $\pm(C+c)$. It can then be shown that, if J is the number of joules equal to one calorie, and r the resistance per unit length of the bar, we have, under suitable conditions, with sufficient accuracy :

$$\frac{2C_\sigma \,.\, d\theta/dx}{c^2 r/J} = \frac{\Delta\theta_T}{\Delta\theta_J}.$$

The temperature gradient $d\theta/dx$ is usually found by a thermocouple which may be inserted in two or more positions along the bar ; usually two bars side by side are used to advantage instead of one.

When we attempt to apply Haga's method to a wire we are confronted with additional difficulties, for it becomes less easy to measure both the temperature variation at the middle and the temperature gradient itself without altering the resistance per unit length of the wire and disturbing the linear heat flow. Briefly, these difficulties are overcome thus :—

(1) Instead of measuring the temperature gradient in any neighbourhood, the difference of temperature between the " ends " of the wire—the same ends across which the electrical resistance is determined—is measured in a similar way to that used by Gray[1] in his heat conductivity experiments on wires. Thus the ratio R/U of the equation below is obtained.

(2) The temperature at the middle is not allowed to alter, Haga's method being employed in the null form used by Berg[2] in his work on plates, and the detector of temperature is a number of turns of the thinnest insulated copper wire used as a resistance thermometer. This method, which Starling[3] first

[1] Gray, " Phil. Trans." A. Part I., p. 165, 1895.
[2] Berg, *loc. cit.*
[3] Starling, " Nature," Feb. 16, 1911.

used to demonstrate the Thomson effect in a red hot iron bar conveying 10 amperes, is found to be sufficiently sensitive with No. 44 wire for measuring absolutely the Thomson effect in wires conveying 3 amperes and heated by steam. The diameters of the bare and double silk-covered detecting wire are only about 0·07 mm. and 0·14 mm. respectively, and the thread-like coil may be wound uniformly on the lathe over the thicker experimental wire (gauge 18, diameter 1·22 mm.), under investigation.

The apparatus used is very simple and will readily be understood from Fig. 1. The wire W under test passes right through

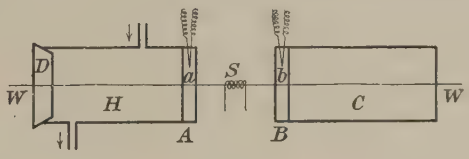


Fig. 1.

the constant temperature sources H and C. H is a cylindrical copper vessel 8 cm. long and of 5 cm. diameter, fitted with vapour inlet and outlet tubes and closed at D by a rubber bung through which the experimental wire W passes easily before being cemented up. C is a rectangular copper vessel 5 cm. square by 10 cm. long, which will hold water or ice. The sides A, B, of H and C respectively are 5 mm. thick and drilled with holes of 1 mm. diameter to admit thermo-junctions at a and b of iron and constantan wire which record the difference of temperature U between the "ends" of the wire under test. The holes a, b, also serve to admit potential leads for measuring the resistance of the wire between its "ends."

Great care is taken in passing and fixing the wire through A and B, as no solder must appear internally, and yet good contact is essential. The side A is made as shown in Fig. 2, the narrow portion being drilled at N with a hole through which the wire just passes. Solder is applied externally through K with a special iron, care being taken that it adheres to the copper as well as the wire under test. B is similarly made, the solder being applied within the vessel C. With practice this fixing of the wire may be done very neatly. The internal length between A and B was usually between 4 cm. and 5 cm., and over about one-third of this length the detecting coil S of copper wire, gauge 44, already alluded to, was symme-

trically wound (previous to fixing the wire), the centre of symmetry lying midway between A and B. The ends of the coil S were brought to terminals on the base board from which they were connected by thicker copper wire, gauge 18, to a resistance bridge arranged as described in section (4) b of this Paper. The resistance of S under the conditions of experiment varied from 5 ohms to 8 ohms. Cotton wool was carefully wound round the operative part of the wire as well as round the temperature sources, H and C. It serves to allay convection currents, and for this reason is essential and, as indicated by the resistance coil S, very considerably diminishes the emissivity loss.

Fundamentally, an experiment is performed thus: Water, either ice-cold or at ordinary temperature, being in the vessel

Fig. 2.

C and steam being circulated through H, a steady current C_1 of from 2·5 to 3·5 amperes is passed through the wire in either direction. If this current is merely reversed the coil S shows a change of resistance, which measures the sensibility, due to a change in the rate of production of Thomson heat; but if, at the same moment that the reversal is made, the current is slightly altered to an appropriate value, C_2, a complete balance may be obtained between the alterations of Joulean and Thomson heat, the coil S then showing no change of temperature. As shown in section 3 below, we then have, under suitable conditions, with sufficient accuracy:—

$$\sigma = \frac{R}{JU}(C_2 - C_1),$$

where U is the difference of temperature between the ends of the wire, R the actual resistance of the wire between these ends under the temperature conditions of the experiment, and J the number of joules equal to one calorie. The Thomson effect σ will then be expressed in calories per coulomb per degree centigrade and, as shown below, its value will be that at the mean temperature $U/2$. The difference of the up-and-down currents, $C_2 - C_1$, called the balancing current, can be measured directly with a milliammeter, or on a Cambridge thermo-electric potentiometer, this measurement and that of R being described in section 4 of this Paper. Owing to the shortness of the wire and the fact that for a balance the temperature at the middle remains constant, such a balance may be found quickly—new steady states being obtained in a few minutes.

In contrasting the conditions of these experiments with those for Gray's conductivity experiments we observe in the present research :—

1. That the quantity of heat passing down the wire has not to be measured, that a small emissivity loss is permitted by the theory, and that error due to the temperature gradient not being quite linear is thus of smaller magnitude. Moreover, the temperature gradient in the strict sense is not required at the middle of the wire, but rather the term U/L of the next section. Probably, therefore, in the present method, a longer wire in proportion to its diameter may be used.

2. Greater care must be taken in this method than in Gray's method in passing the wire through the constant temperature sources. The presence of any solder upon the operative part of the wire would not only alter the resistance per unit length, but might complicate also by the production of Peltier heat. The production of Peltier heat at the actual contact of the wire with the thick copper pieces A and B, presenting such contrast in cross-section with the wire, can easily be shown to have no sensible effect; and the relation between the thermal capacities and thermal conductivities of the thick portions A and B, and those of the wire, together with the manner of passing the wire through and securing its contact, fully justify A and B being regarded as constant temperature ends. With every wire a practical test was made to show that no sensible change of resistance of the detector S resulted on reversing a steady current when H and C were maintained at the same temperature.

3. The Theory of the Method.

(a) *Preliminary Treatment. Ideal Conditions.*

Considering a rod or wire under a temperature gradient, arranged as in Fig. 1, above let all temperatures and temperature-coefficients be dated from the fixed "cold end" taken as zero, and let U be the temperature of the hot end a distance L away.

Let C=electric current in amperes traversing the wire from hot to cold.
S=specific resistance of the material.
K=thermal conductivity of the material.
A=area of cross-section of wire.
p=perimeter of wire.
α=temperature coefficient of resistance.
σ=Thomson effect, assumed positive and at first constant.
E=heat loss per square centimetre per sec. per 1°C. excess temperature above the enclosure.
θ_0=temperature of enclosure.
J=number of joules equivalent to one calorie.
θ=temperature at a distance x from the hot end.

The differential equation expressing the distribution of temperature may be written :—

$$\frac{d^2\theta}{dx^2}+a\cdot\frac{d\theta}{dx}+b\theta=c,$$

where the Thomson heat term $a=-C\sigma/KA$

the emissivity term $b=\left[\frac{C^2S\alpha}{JA}-Ep\right]/KA,$

the Joulean heat term $c=-\left[\frac{C^2S}{JA}+Ep\theta_0\right]/KA.$

The general solution under the present end conditions is :—

$$\theta=\frac{c}{b\sinh\lambda L}\left[e^{\frac{-ax}{2}}\sinh\lambda(x-L)-e^{\frac{-a}{2}(x-L)}\sinh\lambda x\right]+\frac{c}{b}$$
$$-\frac{U}{\sinh\lambda L}e^{\frac{-ax}{2}}\sinh\lambda(x-L),$$

where $\lambda=\sqrt{(a^2-4b)}/2.$

But if, as is nearly always justifiable, $aL/2$ may be taken as small compared with unity, and if in addition the emissivity

term b is so small that terms in $a \,.\, b$ and $c \,.\, b$ may be neglected in comparison with a and c respectively, we have

$$\theta = U\left(\frac{L-x}{L}\right)\left(1-\frac{ax}{2}\right)+U\left(\frac{L-x}{L}\right)\frac{bx}{6}(2L-x)-\tfrac{1}{2}cx(L-x).$$

When a current C_1 is passing from hot to cold put $\theta=\theta_1$; $c=c_1$; $b=b_1$; and $a=a_1=-C_1\sigma/KA$; and when a current C_2 is passing from cold to hot put $\theta=\theta_2$; $c=c_2$; $b=b_2$; and $a=a_2=+C_2\sigma/KA$.

The temperature change on reversing the current C_1 and increasing its value to C_2 is thus given by:—

$$d\theta = U\left(\frac{L-x}{L}\right)\frac{x}{2}(-a_2+a_1)+U\left(\frac{L-x}{L}\right)\frac{x}{6}(2L-x)(b_2-b_1) -\tfrac{1}{2}x(L-x)(c_2-c_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If this is zero at the middle where $x=L/2$, we obtain:

$$\sigma=\frac{LS}{UJA}(C_2-C_1)(1+\tfrac{1}{2}aU) \quad . \quad . \quad . \quad . \quad (2\text{A})$$

$$=\frac{R_0}{JU}(C_2-C_1)\left(1+a\frac{U}{2}\right) \quad . \quad . \quad . \quad . \quad . \quad (2\text{B})$$

$$=\frac{R}{JU}(C_2-C_1) \text{ very approximately,} \quad . \quad (2\text{C})$$

where R_0 is the resistance of the actual wire when at the temperature of the cold end and R its resistance when under temperature gradient.

Conversely when the current C_2 is so chosen that at the middle $d\theta$=zero and relation (2) holds, we have (on substituting in equation (1)) for $d\theta$ elsewhere:—

$$d\theta = U\left(\frac{L-x}{L}\right)\frac{x}{2}\left(\frac{L-2x}{6}\right)(b_2-b_1)$$

$$=U\left(\frac{L-x}{L}\right)\frac{x}{12}(L-2x)\frac{Sa}{JA\,.\,KA}(C^2{}_2-C^2{}_1).$$

Thus, if a is zero, the balance is not only in the middle but everywhere. If a is not zero, the deviation is symmetrical about the middle and can easily be shown to be very slight, compared with the temperature changes which result on merely reversing the current, but not increasing its magnitude. Thus under the conditions assumed above the detecting coil may have appreciable length if symmetrically wound about the middle; moreover, errors due to lack of perfect symmetry will be very small.

(*b*) *Complete Theory: Special Conditions Necessary for Wires.*

While in general, in work on the Thomson effect, the "a" term, equal to $-C\sigma/KA$, may be taken as small compared with unity, on the other hand, the neglect of products of the "a," "b" and "c" terms is often not justifiable. When dealing with wires it is more necessary than ever to pay special attention to these points, and the following form the chief consideration of this section :—

(i.) The effect of a temperature coefficient of the Thomson effect.

(ii.) The effect of a rise of the emissivity loss on both the accuracy and sensibility.

(iii.) The effect of a rise of Joulean heat.

(iv.) The effect of the length of the detecting coil when product terms are considered and σ is a variable.

(v.) The effect of a rise of the Thomson heat or "a" term towards unity.

Assuming that over the range of temperature between the hot and cold ends the variation of σ is linear, we may write, dating temperatures from the cold end as before

$$\sigma_\theta=\sigma(1+\beta\theta).$$

and the differential equation of temperature distribution becomes—

$$\frac{d^2\theta}{dx^2}+a(1+\beta\theta)\frac{d\theta}{dx}+b\theta=c.$$

Still assuming a to be small compared with unity, but otherwise carrying the expansion much further, we obtain the solution—

$$\theta=U\left(\frac{L-x}{L}\right)\left(1-\frac{ax}{2}\right)-\frac{U^2a\beta}{6L^2}x(L-x)(2L-x)+\frac{Ub}{6L}x(L-x)(2L-x)$$
$$-\frac{Uab}{12L}x^2(L-x)(2L-x)-\tfrac{1}{2}cx(L-x)+\frac{bc}{24}x(L-x)(x^2-xL-L^2)$$
$$-\frac{ac}{12}x(L-x)(L-2x)+\frac{abc}{720}x(L-x)(L-2x)(6x^2-6Lx-7L^2) \quad (3)$$

and hence, using the same notation as before, on changing from a current $+C_1$ to a current $-C_2$, we obtain :—

$$d\theta=\frac{U}{2L}x(L-x)(-a_2+a_1)+\frac{U^2\beta}{6L^2}x(L-x)(2L-x)(-a_2+a_1)$$
$$+\frac{Ux}{6L}(L-x)(2L-x)(b_2-b_1)+\frac{U}{12L}x^2(L-x)(2L-x)(-a_2b_2+a_1b_1)$$
$$+\tfrac{1}{2}x(L-x)(-c_2+c_1)+\frac{x}{24}(L-x)(x^2-xL-L^2)(b_2c_2-b_1c_1)$$
$$+\frac{x}{12}(L-x)(L-2x)(-a_2c_2+a_1c_1)+\frac{x}{720}(L-x)(L-2x)$$
$$(6x^2-6Lx-7L^2)(a_2b_2c_2-a_1b_1c_1) \quad . \quad (4)$$

Equating this to zero and simplifying :—

$$(a_2-a_1)\left\{1+\frac{\beta U(L-x)}{L}-\frac{U\beta}{3L}(L-2x)\right\}$$
$$=\frac{2L-x}{3}(b_2-b_1)+\frac{L}{U}(c_1-c_2)+\frac{x}{6}(2L-x)(a_1b_1-a_2b_2)$$
$$+\frac{L}{12\,.\,U}(x^2-xL-L^2)(b_2c_2-b_1c_1)+\frac{L}{6U}(L-2x)(a_1c_1-a_2c_2)$$
$$+\frac{L}{360\,.\,U}(L-2x)(6x^2-6Lx-7L^2)(a_2b_2c_2-a_1b_1c_1) \quad . \quad . \quad (5)$$

An examination of the left-hand side of this equation at once shows that a thermo-junction at the middle of the gradient or a detecting coil symmetrically wound about the middle will respond to the value of σ at this middle temperature. Putting $x=L/2$ we find :

$$(a_2-a_1)(1+\beta\theta)=\frac{L}{2}(b_2-b_1)-\frac{L}{U}(c_2-c_1)+\frac{L^2}{8}(a_1b_1-a_2b_2)$$
$$+\frac{5L^3}{48\,.\,U}(b_1c_1-b_2c_2)\,. \quad (5A)$$

which, on substituting for the a, b and c terms and writing b for $(b_1+b_2)/2$ and $c=(c_1+c_2)/2$ becomes very approximately :—

$$\sigma_\theta=\frac{R_0}{JU}(C_2-C_1)\left(1+\frac{aU}{2}\right)-\frac{b\sigma L^2}{8}+\frac{5L^2}{48}\,.\,\frac{R_0}{JU}(C_2-C_1)(b-ac)$$

or very approximately.

$$\sigma_\theta=\frac{R_0}{JU}(C_2-C_1)\left(1+\frac{aU}{2}\right)-\frac{b\sigma L^2}{48}\,. \quad . \quad . \quad . \quad . \quad (6)$$

Hence, as b is negative, if the length of wire is increased or the protection diminished, so that b becomes of appreciable value, the values of σ obtained by neglecting it will become too low. The effect of the guard-ring of cotton wool in diminishing b is very great—as may be judged by the change of resistance of the detecting coil on removing it—but experiments were performed with constantan wire of different lengths (the metal for which b is greatest) to show that in the main experiments the lengths of wire were sufficiently short for the correcting term to be neglected.

The effect of a rise of emissivity is also to diminish the sensibility which is measured by the change of temperature at the middle, on reversing, but not altering, the magnitude of a mean current $C=(C_1+C_2)/2$. Putting $a_2=-a_1=+C\sigma/KA$,

$b_1=b_2=b$, $c_1=c_2=c$, and $x=L/2$ in equation (4), and neglecting variations of σ with temperature, we obtain for the sensibility :—

$$d\theta=\frac{ULC\sigma}{4KA}\left(1+\frac{bL^2}{8}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Though an increase in L within the limits allowed by the emissivity loss increases the sensibility any such benefit is in great part lost by the increase in time needed for the attainment of the steady state. An increase in U is also undesirable and unnecessary, the smallness of A giving satisfactory sensibility even with moderate currents.

From equation (5A) it is easy to see that a rise of the c term embracing Joulean heat is—unlike a rise in the b term—quite unimportant both from the standpoints of error and sensibility.

It is important to study the effect of increasing the length of the detecting resistance coil beyond the immediate neighbourhood of the middle of the wire, thereby obtaining a greater absolute change of resistance on reversing an electric current through the wire under test.

Let d=length of detecting coil symmetrically wound about the middle. Then the average temperature to which it corresponds is given by :—

$$\varphi=\frac{1}{d}\int_{\frac{L-d}{2}}^{\frac{L+d}{2}}\theta \,.\, dx.$$

Passing a current C_1 in the positive direction, writing $a=a_1$, $b=b_1$, $c=c_1$, and integrating the expansion for θ of equation (3) we have :—

$$\varphi_1=\frac{U}{2}-a_1\frac{UL}{8}\left(1-\frac{d^2}{3L^2}\right)+b_1\,.\,\frac{UL^2}{16}\left(1-\frac{d^2}{3L^2}\right)$$
$$-\tfrac{1}{8}c_1L^2\left(1-\frac{d^2}{3L^2}\right)-\frac{a_1b_1U}{12L}\left(\frac{45L^4-20L^2d^2+3d^4}{240}\right)$$
$$-b_1c_1\left(\frac{25L^4-10L^2d^2+d^4}{1920}\right). \quad . \quad . \quad . \quad . \quad . \quad (8)$$

the term a_1 including β the Thomson effect coefficient and standing for $\frac{-C_1\sigma}{KA}\left(1+\beta\,.\,\frac{U}{2}\right)$. A similar expression is ob-

tained for φ_2 on passing a current C_2 in the opposite direction, whence

$$\varphi_2-\varphi_1=-(a_2-a_1)\frac{UL}{8}\left(1-\frac{d^2}{3L^2}\right)+(b_2-b_1)\frac{UL^2}{16}\left(1-\frac{d^2}{3L^2}\right)$$
$$-(c_2-c_1)\frac{L^2}{8}\left(1-\frac{d^2}{3L^2}\right)-(a_2b_2-a_1b_1)\frac{U}{12L}\left(\frac{45L^4-20L^2d^2+3d^4}{240}\right)$$
$$-(b_2c_2-b_1c_1)\left(\frac{25L^4-10L^2d^2+d^4}{1920}\right). \quad . \quad . \quad . \quad (9)$$

Equating to zero and dividing throughout by $\frac{UL}{8}\left(1-\frac{d^2}{3L^2}\right)$ we have :—

$$a_2-a_1=\frac{L}{2}(b_2-b_1)-\frac{L}{U}(c_2-c_1)-\frac{1}{12}\cdot\frac{1}{L^2}\cdot\frac{1}{30}(a_2b_2-a_1b_1)$$
$$\left(\frac{45L^4-20L^2d^2+3d^4}{1-d^2/3L^2}\right)$$
$$-\frac{1}{LU}\cdot\frac{1}{240}(b_2c_2-b_1c_1)\left(\frac{25L^4-10L^2d^2+d^4}{1-d^2/3L^2}\right).$$

Substituting for the a, b and c terms, and in the last two terms neglecting α and β and writing b for $(b_1+b_2)/2$ we have the very approximate expression :—

$$\sigma_\theta=\frac{R_0}{JU}(C_2-C_1)\left(1+\frac{aU}{2}\right)-\frac{b\sigma}{720}\frac{1}{L^2}\left(\frac{15L^4-10L^2d^2+3d^4}{1-d^2/3L^2}\right). \quad (10)$$

The correcting term in b becomes $-b\sigma L^2/48$ for d=zero, $-b\sigma L^2/50$ for $d=L/3$, $-b\sigma L^2/52$ for $d=L/2$, and $-b\sigma L^2/60$ for $d=L$. The effect of the detecting coil is thus small but helpful in diminishing the effect of emissivity.

The assumption that the a term, *i.e.*, $C\sigma/KA$ is small compared with unity is, of course, justifiable in nearly all ordinary work where rods are used. Though L is small in the case of wires, the smallness of A is such as to render an investigation most desirable. The general case is complicated, but, by neglecting β the Thomson effect temperature coefficient, and assuming b the emissivity loss to be rendered negligible, the effect of a rise of $La/2$ may be studied. The general solution for θ is then :—

$$\theta=U\left(\frac{e^{-ax}-e^{-aL}}{1-e^{-aL}}\right)+\frac{cx}{a}-\frac{cL}{a}\left(\frac{1-e^{-ax}}{1-e^{-aL}}\right).$$

The author is indebted to Miss M. L. Humby, B.Sc., for the following solution obtained by the use of Bernouilli's numbers :

$$\theta=\frac{U(L-x)}{L}\left\{1-\frac{x}{2}a-\frac{x(L-2x)}{12}a^2+\frac{x^2(L-x)}{24}a^3 + \frac{x(L-2x)(L^2+3Lx-3x^2)}{720}a^4+\ldots\ldots\right\}$$
$$+c(L-x)\left\{-\frac{x}{2}-\frac{x(L-2x)}{12}.a+\frac{x^2(L-x)}{24}.a^2 + \frac{x(L-2x)(L^2+3Lx-3x^2)}{720}.a^3+\ldots\ldots\right\}$$

With the usual notation we may obtain $\theta_2-\theta$, the difference of temperature which results on changing from a current $+C_1$ to a current $-C_2$, and equating this to zero and simplifying we find :—

$$a_2-a_1=-\frac{L-2x}{6}(a_2-a_1)(a_2+a_1)+\frac{x(L-x)}{12}(a_2-a_1)(a_2^2+a_1a_2+a_1^2) + \frac{(L-2x)(L^2+3Lx-3x^2)}{360}(a_2^2+a_1^2)(a_2-a_1)(a_2+a_1) - \frac{L}{U}(c_2-c_1)$$
$$-\frac{L}{U}\left(\frac{L-2x}{6}\right)(a_2c_2-a_1c_1)+\frac{L}{U}x\left(\frac{L-x}{12}\right)(a_2^2c_2-a_1^2c_1) + \frac{L}{U}\frac{(L-2x)(L^2+3Lx-3x^2)}{360}(a_2^3c_2-a_1^3c_1).$$

Putting $x=L/2$ and causing symmetrical terms about the middle to vanish, we find on substituting for a and c :—

$$\sigma=\frac{R}{JU}(C_2-C_1)+\frac{L^2}{48}\cdot\frac{\sigma^3}{K^2A^2}(C_2^2-C_1C_2+C_1^2)-\frac{L^2}{48}\cdot\frac{R}{JU}\cdot\frac{\sigma^2}{K^2A^2}(C_2-C_1)(C_2^2+C_1^2)$$

which leads to :—

$$\sigma=\frac{R}{JU}(C_2-C_1)-\frac{L^2}{48}\sigma^3\frac{C_1C_2}{K^2A^2}.$$

Calling $C_1C_2/K^2A^2=C^2/K^2A^2$, where $C=\sqrt{C_1C_2}$, and $a=C\sigma/KA$, we obtain :—

$$\sigma\left(1+a^2\cdot\frac{L^2}{48}\right)=\frac{R}{JU}(C_2-C_1). \quad \ldots\ldots \quad (11)$$

So an error due to the rise of a or $C\sigma/KA$ towards unity is not important until $L^2a^2/48$ rises towards unity.

4. The Practice of the Method.

(*a*) *The Measurement of* $C_2 - C_1$ *the Balancing Current.*

The method of measuring the excess current $C_2 - C_1$ which will just balance the change of Thomson heat on reversing the main current will readily be understood from Fig. 3 below.

The main circuit consists of accumulators (10 or 12 volts), an ammeter, rheostats, the reversing switch K_1, the apparatus E with the wire under test and the special resistance R. The reversing switch K_1 was specially designed to be of negligible resistance so that the current should not alter appreciably on making a reversal even under low voltages—most mercury commutators being untrustworthy in this respect. The special resistance frame R consists of two thick constantan wires, each of about 1 ohm resistance stretched across stout copper pieces well supplied with terminals as shown. Its object

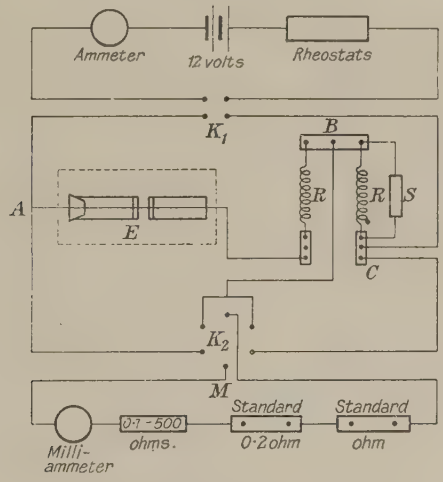


Fig. 3.

is to supply the main circuit with two exactly equal resistances, the one including the experimental wire and extending from A to B in the diagram, and the other from B to C. By means of the special switch K_2 of negligible resistance either of these equal resistances can be shunted through the branch circuit M. This latter consists of a resistance box, a rheostat, a milliammeter, and a standard 0·2 ohm, with potential leads for calibrating the milliammeter directly on a Cambridge thermoelectric potentiometer reading to 30 millivolts : on the same

potentiometer, the 0·2 ohm could be compared with a standard 1 ohm. The equality of the two resistances A–B and B–C can be tested by the equality of full deflections of the milliammeter for both sides of the rocking key K_2—the fine adjustment being effected with the aid of the high resistance shunt rheostat S. As either A–B or B–C is always shunted, the current through the main circuit will remain constant, no matter in which direction it is flowing, and on transferring the shunt circuit M from AB to BC by the rocker K_2 the current flowing through E the wire under test will be greater than before by the reading of the milliammeter.

The keys K_1 and K_2 were side by side and could be switched over simultaneously, in which case in general the detecting coil S of Fig. 1 would indicate a change of temperature unless the changes of Joulean and Thomson heat were perfectly balanced. The milliamperes required for a balance give $C_2 - C_1$ of the formula for σ.

(*b*) *The Detection of Change of Temperature in the Middle of the Wire.*

The terminals of the copper resistance detector S of Fig. 1 were joined by thick copper leads to a Post Office box with 10 and 1,000 ratio arms arranged for maximum sensibility as in Fig. 4. The battery was a 2-volt accumulator, and was allowed

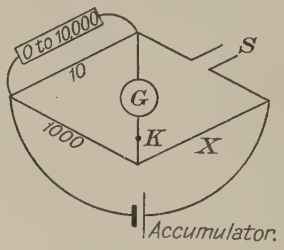


Fig. 4.

to give a continuous current throughout the experiment so that the slight heating effect in the thermometer coil S should be constant. By balancing first to the nearest ohm and then shunting the 10 ratio arm with a high resistance it could easily be arranged that on depressing the galvanometer key no deflection resulted. On reversing the main current through the wire under test and switching over K_2 of Fig. 3 simultaneously, and again, after a minute, depressing the galvanometer

key, there was in general a deflection unless the Thomson heat was exactly balanced by the small current registered by the milliammeter. The galvanometer was a low resistance quartz fibre instrument of the Broca type, 1 micro-ampere, producing some 13 cm. deflection on the distant scale.

(c) *The Measurement of U the Temperature Difference Between the Ends of the Wire.*

The temperature difference U will be somewhat smaller than the difference of temperature between the steam in H and the water in C of Fig. 1. It was measured by an iron-constantan thermocouple insulated with special varnish, the junctions being well inserted in the holes a and b of Fig. 1, which contain a little mercury. The thermocouple gave 54·38 microvolts per degree between 0°C. and 100·15°C. and 54·92 microvolts per degree between 21·64°C. and 100·15°C. The constantan wires were joined together and the iron wires to copper leads, these latter junctions lying side by side in tubes containing paraffin oil and immersed in a large water bath. The copper leads were joined to the Cambridge thermo-electric potentiometer and the microvolts read off directly. U only differed by 0·2°C. to 0·3°C. from the temperature interval between the steam and the water.

(d) *The Measurement of the Resistance of the Wire Between its Ends.*

Owing to the small temperature coefficient of the alloys used in this research it was sufficiently accurate to find the resistance of a long length of the wire giving an exact balance on an accurate Post Office box, and to measure the length of the experimental wire between its ends, as in Gray's experiments, to about 0·1 mm.

It was found, however, that the resistance of the actual wire could easily be measured in situ by treating it as a low resistance and using the mercury holes a and b of Fig. 1 for the insertion of potential leads. A current of the nominal value 1·018 amperes—which gave a P.D. across a standard ohm. sufficient to balance a Weston cell—could easily be sent through the wire in either direction, while the millivolts across a and b were measured directly on the thermo-electric potentiometer. The good agreement between the two methods is important in showing good contact, definite ends, and smallness of end

correction. The balance on the potentiometer was also almost identically the same whether the current was let directly into the wire or in at a terminal on the steam heater except in one case, where the solder was found not to have taken to the copper. It will probably be possible to measure in this way the actual resistance of a wire of normal temperature coefficient under actual temperature gradient provided the mean of the millivolts be taken resulting from the interchange of the potential leads and the reversal of the main current.

By using the same standard ohm in the manners indicated, both as a basis for calibrating the milli-ammeter or measuring C_2-C_1, and also as a means of obtaining a known current for the measurement of R the resistance of the wire, it is noteworthy that its actual value disappears from the calculation for σ and that the accuracy of the potentiometer becomes the important factor.

(*e*) *The Sensibility of the Balance, the Rapidity of Working, and the Attainment of the Balance.*

When the apparatus of Fig. 1 was fitted with a constantan wire of length 4 cm., supplied with steam and ice so that $U=100°$C. approximately, and was traversed by a current of 3·5 amperes, a full scale deflection of 50 cm. was obtained in just over a minute if the current was merely reversed but not altered in magnitude. Using steam and water at 22°C. and reversing a current of 3 amperes, 30 cm. deflection was obtained in 1 minute and 37 cm. in 2 minutes. With German-silver of the same length, 100°C, interval, and 3·5 amperes 18 cm. deflection was observed in a minute. In manganin the Thomson effect is feeble, viz., 0·68 micro-calorie per coulomb, but for $U=81°$C. a reversal of the same current yielded 5 cm. deviation in the first minute.

This sensibility is very satisfactory, and in further work the author hopes to increase it. Moreover, as the steady state is attained so rapidly it is unnecessary to duplicate by use of a second parallel wire—indeed, such duplication would add difficulties—for, in the short time needed for testing a balance, change of temperature of the detecting coil due to other causes is normally inappreciable. The time of attainment of a new steady state probably shortens on nearing a balance, for in the limit, when the balance is perfect, the middle is a point of stationary temperature and the length of wire is in this respect virtually halved.

Practically the sensibility is not purely a function of the current and temperature difference even for the same wire; for such variable features as the stability of zero of the galvanometer or the steadiness of the sources or "progressive changes" all influence the precision of balance. For example, though U was greater when ice was used instead of ordinary water, the slow progressive rise of temperature of the tank in the former case rendered a balance more difficult and often less precise.

The balance is best approached from both sides by trying first the effect of too big and then of too small a shunt current. After balancing the galvanometer and switching over K_1 and K_2 simultaneously the galvanometer key may again be depressed in about 30 seconds and a movement of the needle looked for. When approaching closely the exact balancing current several reversals should be made so as to make sure that any slight movement of the galvanometer line of light is reversible and not due to a slight progressive change of temperature. Such progressive changes have always caused trouble to experimenters on the Thomson effect. They are due, among other things, to variations in temperature of the hot and cold sources, to insufficient protection of the wire from convection currents, to variation of the main current and the room temperature and to local thermo-electric effects; they may be reduced greatly by special attention to these points and by duplicating the apparatus, but nothing tends more towards their elimination than securing rapidity of attainment of the steady state.

The balance was unaffected if the current instead of entering the steam chamber by the wire under test entered by a terminal on the steam heater.

5. Results of Experiments.

The results of all experiments are tabulated in Table I.

The resistances of the wires used are shown in Table II. The values in the last column obtained by the potentiometer method were those used in the calculation of σ. The resistance values correspond to 20°C. approximately.

In this preliminary work with alloys, the small temperature coefficients were neglected in the calculation of σ the Thomson effect. The best experiments show σ for the constantan used

TABLE I.—*Values of* σ.

Material and number of experiment.		U	Main current amperes.	Balancing current in milliamperes.	Temp. at which σ is found.	$\sigma \times 10^6$ in calories per coulomb.
Constantan A $L=4{\cdot}0_2$	1	78·5	2·0	88 ± 1	60	$-4{\cdot}7_3$
	2	77·2	2·75	88 ± 1	61	$-4{\cdot}8_1$
	3	76·5	3·5	$86{\cdot}5\pm0{\cdot}5$	61	$-4{\cdot}7_7$
	4	78·1	2·75	87 ± 1	61	$-4{\cdot}7_0$
	5	78·3	3·5	$87{\cdot}7\pm0{\cdot}2$	61	$-4{\cdot}7_2$
	6	78·4	3·0	$87{\cdot}5\pm0{\cdot}5$	61	$-4{\cdot}7_0$
	7	78·0	3·5	$87{\cdot}5\pm0{\cdot}5$	61	$-4{\cdot}7_3$
	8	99·4	3·0	111 ± 1	50	$-4{\cdot}7_1$
	9	99·5	3·5	$111{\cdot}5\pm1$	50	$-4{\cdot}7_2$
	10	99·6	3·0	111 ± 1	50	$-4{\cdot}7_0$
	11	99·7	3·5	$110{\cdot}5\pm1$	50	$-4{\cdot}6_7$
Constantan B $L=4{\cdot}4_5$	1	80·0	3·5	$80{\cdot}0\pm0{\cdot}5$	60	$-4{\cdot}7_0$
	2	79·3	3·0	$80{\cdot}0\pm1$	60	$-4{\cdot}7_4$
	3	99·6	3·0	100 ± 1	50	$-4{\cdot}7_2$
Constantan C $L=4{\cdot}9_0$	1	79·5	3·5	$73{\cdot}4\pm0{\cdot}5$	60	$-4{\cdot}6_9$
	2	79·8	3·0	$73{\cdot}4\pm0{\cdot}5$	60	$-4{\cdot}6_7$
Constantan D $L=5{\cdot}9_7$	1	83·7	3·5	$64{\cdot}1\pm0{\cdot}5$	58	$-4{\cdot}7_8$
	2		*See* Note below			
German Silver G $L=4{\cdot}0_6$	1	77·8	3·0	$87{\cdot}5\pm1{\cdot}5$	61	$-2{\cdot}3_3$
	2	78·6	3·5	$89{\cdot}0\pm1$	60	$-2{\cdot}3_5$
	3	99·3	3·0	$110{\cdot}5\pm1$	50	$-2{\cdot}3_1$
	4	99·3	3·5	109 ± 1	50	$-2{\cdot}2_7$
Manganin M $L=4{\cdot}0_2$	1	80·7	3·5	$15{\cdot}4\pm0{\cdot}5$	60	$+0{\cdot}6_8$
	2	81·7	3·0	$15{\cdot}4+0{\cdot}5$	60	$+0{\cdot}6_7$

Experiment C_2 was only a retest of balance performed an hour later under 3 amperes. The result of experiment D yielding a higher value was surprising when a lower value was expected; nevertheless, the balance was very definite. Perhaps the rise of the "a" term had more effect than the emissivity loss. On removing nearly all the cotton wool a much lower balancing current—about 60 milliamperes—was required but convection currents then prevent precise measurement.

TABLE II.—*Resistances at* 20°C. *of Wires Employed.*

Material.	Length in cm.	Resistance calculated from value per unit length	Resistance found on thermoelectric potentiometer.
		ohms.	ohms.
Constantan A.....	$4{\cdot}0_2$	$0{\cdot}0173_6$	$0{\cdot}0176_2$
Constantan B.....	$4{\cdot}4_5$	$0{\cdot}0192_2$	$0{\cdot}0196_5$
Constantan C ...	$4{\cdot}9_0$	$0{\cdot}0211_6$	$0{\cdot}0212_4$
Constantan D.....	$5{\cdot}9_7$	$0{\cdot}0257_8$	$0{\cdot}0261_2$
Manganin M	$4{\cdot}0_2$	$0{\cdot}0147_2$	$0{\cdot}0148_2$
German Silver G	$4{\cdot}0_0$	0·00864	0·00866

to be about $-4{\cdot}7_2 \times 10^{-6}$ calories ($J_{20}=4{\cdot}18$) per coulomb per 1°C. at 60°C. The corresponding values for German silver and manganin are $-2{\cdot}3_5$ and $+0{\cdot}6_8$ micro-calories respectively.

6. Conclusion.

The method appears promising on account of its simplicity, rapidity and sensitiveness, the detector, unlike a thermo-junction, producing no distortion or alteration of electrical resistance at the critical place. The limit of accuracy attainable will probably be found to be associated with thermal and electrical "end-correction." That the Peltier effect has negligible influences is confirmed by König ("Phys. Zeits." 17, June 1, 1916) in a very recent Paper, and additional practical tests of this point are in view by the author. A new apparatus suitable for temperature coefficient work is in the process of design, and the author hopes to carry out the intention expressed in section I. as soon as conditions improve; bismuth wire of the desired gauge is not obtainable at present.

The author must express his thanks to Miss E. M. Humby for valuable mechanical help when difficult to obtain, and especially for services rendered in the successful fixing of the wires through the constant temperature sources. He is also indebted to Dr. A. Griffiths for placing at his disposal for so long a time so much of the best electrical apparatus in the physics department. The expenses of this research were completely defrayed by a grant from the Dixon Fund, University of London, for which the author is very grateful to the Senate.

Summary.

This Paper describes how absolute measurements of the Thomson effect may be made in wires. The theory is fully worked out and the sources of error likely to arise—owing especially to the smallness of the area of cross-section—are considered. The method is sensitive, consistent, and very rapid and the ultimate object is to determine the Thomson effect at different temperatures in a number of metals, both rare and base, at the same time and with the same specimens finding their thermo-electric powers. The preliminary experiments of this Paper, testing the method, are with constantan wires of different lengths, with manganin, and with German silver.

DISCUSSION.

Mr. F. E. Smith suggested that the method might have been modified by having two exactly similar systems arranged in opposite arms of a Wheatstone bridge, so that the current passed from hot to cold in one wire and from cold to hot in the other. Any change in the relative temperatures of the two wires on reversing the current would be indicated by the bridge being thrown out of balance. This seemed preferable to measuring the temperature of a wire by the resistance of another wire wound round it.

Mr. D. Owen thought the method was very satisfactory. Had the author thought of using electrical heating for the hot end in order to get smaller temperature gradients, in view of the high sensibility of the arrangement? He thought the figures of Oosterhuis stood in need of verification. If the author could adapt his method to deal with crystals, such as were employed in wireless detectors, the results would be of very great interest.

Dr. R. S. Willows said that it was difficult to see from the equations which Mr. Nettleton had put down on the board whence the energy was derived in cases such as those mentioned in the Paper which Mr. Darling was about to read. In some of these cases dE/dT and d^2E/dT^2 were both zero. It would be useful if the method could be rendered applicable to substances with large temperature coefficients.

Prof. W. Eccles said he had hoped that the author would have explained just what the important points of the method were in a less abstract manner—with the aid, say, of diagrams of the temperature conditions along the wire before and after the current reversal.

The Author, in a written reply, thanks Mr. F. E. Smith for his suggestion, which, however, as regards sensibility, would depend on the value of the temperature coefficient of resistance, and might carry with it additional complications such as those which enter into King's experiments. In reply to Mr. Owen, the use of electrical heaters would simplify temperatur coefficient work enormously, but unfortunately there are mechanical difficulties arising out of the facts that the solder fixing the wire must be applied from behind, and that, in order that the resistance of the wire may be measured as a low resistance in situ, the copper must be narrowed down, as shown at K in Fig. 2, leaving a very small bearing surface at N. The author still hopes that he may be able to overcome these difficulties, while ensuring at the same time that the difference of temperature U, measured by the thermocouple, is substantially that between the extremities of the wire. He agrees with Mr. Owen that the results of Oosterhuis should be confirmed, as well as those of Aalderink, in view of the extraordinary conclusions to which they lead; at the same time, he has a very high opinion of the methods adopted at Groningue, and his own results on mercury some time ago were not very different from those of Schoute In reply to Prof. Eccles, the author has himself felt the difficulty of explaining the essence of the method simply and satisfactorily. Graphs of the distribution of temperature afford little help. What is actually done is explained in a few words in section 2 of the Paper, though no simple proof of the formula is given. A "proof" of the formula $\sigma=R(C_2-C_1)/SU$ is obtained very simply by equating the electrical heat produced per second per centimetre—viz., $C_1^2R/SL + C_1\sigma U/L$, when C_1 is passing from hot to cold, to that produced when C_2 is passing in the opposite direction—viz., $C_2^2R/SL - C_2\sigma \cdot U/L$. This proof was omitted not so much because it assumes that σ, R and the temperature gradient are constant everywhere, and ignores emissivity, as because it neglects thermal conductivity, or assumes that Joulean and Thomson heat are propagated similarly. In reply to Dr. Willows, the method is equally applicable to wires of large temperature

coefficient. Equation (2B) may then be applied, or equation (2C) if the resistance of the wire be measured directly while under temperature gradient, as suggested in section 4D. The author has no satisfactory explanation of the energy problems arising out of the researches in Holland, or those arising from Mr. Darling's experiments: in the absence of measurements of σ and π there are few data to go upon. In the case of Mr. Darling's experiments, it must be remembered that though with, say, the bismuth silver couple over the range 300°C.-500°C., both dE/dt and d^2E/dT^2 are zero, no additional energy or thermo-electric force is manifest. If the law of successive temperatures is true with Mr. Darling's materials, a thermocouple composed of molten bismuth and silver with one junction at 300°C. and the other at 400°C. or 500°C., should show no E.M.F., corresponding to zero Peltier effects and equality of Thomson coefficients.

V.—*On the Thermo-electric Properties of Fused Metals.* By Charles Robert Darling, *A.R.C.S., F.I.C., and* Arthur W. Grace.

Received October 30, 1916.

1. *Bismuth.*

In measuring high temperatures by the thermo-electric method, it has hitherto been customary to regard the melting point of either member of the couple as the extreme temperature capable of being measured. As pyrometers of this type are now constructed, the fusion of either metal causes a break in the circuit, and hence for temperatures exceeding 1,000°C. it has been found necessary to use junctions of platinum and an alloy of platinum and rhodium. If, however, a pyrometer could be arranged so that the fusion of either member of the junction would not destroy the circuit, it might be possible to use cheap metals over very high ranges of temperature, provided the boiling points were not too nearly approached. The boiling points of metals have been investigated by Greenwood, who has shown that the values for common metals frequently exceed 2,000°C.; tin, for example, boiling at 2,270 deg., copper 2,310 deg., and iron 2,450 deg. It would, therefore, appear feasible, in a specially designed pyrometer, to measure temperatures as high as 1,500 deg., and probably higher, by using common metals in the molten condition, provided their thermo-electric properties were suitable. Further, in the case of bismuth, which boils at 1,420 deg., the high E.M.F. developed when this metal is joined to iron, copper, &c., suggests the possibility of delicate measurements over a range from 0 deg. to 800 deg. or 1,000 deg., again assuming that the thermo-electric properties after fusion are satisfactory.

With these objects in view an investigation was commenced by the first-named author about three years ago, but owing to the abnormal conditions prevailing, progress has been very slow. As a preliminary, it was necessary to determine whether any notable change in thermo-electric properties was caused by fusion, and the results arrived at in this connection were given at the meeting of the Society held on June 30th, 1916. It was then shown that in the cases of lead, tin, zinc and cadmium, using a variety of metals as second members of the junctions, that no perceptible break occurred in the continuity of the curves obtained by plotting E.M.F. against temperature,

either at fusion or at any subsequent stage up to 700°C. With bismuth, however, several cases were noted in which the E.M.F. remained nearly constant after fusion over a wide range of temperature, reproducing the phenomenon of thermo-electric " halt " observed by Barrett* with a junction of iron and an alloy of iron, nickel and manganese containing 1·2 per cent. of carbon. This property of molten bismuth has since been more carefully examined, and also the behaviour of molten bismuth in cases where this halt is not obtained ; and the present Paper is devoted to the special case of bismuth. Work is being carried on, as circumstances permit, with a view to accomplishing the main object of the research, and it is hoped to communicate the results at a later date.

Historical.

The effect of fusion in the case of an iron-bismuth junction was first observed by von Obermayer in 1872†. The bismuth was placed in a funnel provided with a long stem, and a junction formed at the upper and lower end, and the upper layer of bismuth in the conical part was melted by heating this portion of the funnel. A complicated method for measuring the thermo-electric change was used, in which values were referred to a copper-german silver element. A falling-off in E.M.F. was noted after fusion.

Further observations on similar lines were made by Minarelli in 1875,‡ who found that with junctions of Bi-Fe and Bi-Pt the E.M.F. diminished after fusion, whereas with Bi-Cu the effect of fusion was to slow down the rate of increase. Observations were made up to 380°C. with Bi-Fe and Bi-Cu ; and up to 500 deg. with Bi-Pt. The results obtained suffered from the absence of an accurate method of measuring the E.M.F. developed.

No systematic examination of the thermo-electric properties of fused bismuth appears to have been made since this date, although one or two isolated results have been recorded bearing on the effect of fusion, but not upon the properties of the liquid metal at temperatures much higher than its melting point (269°C.). Thus K. Siebel§ found that with a manganin-bismuth junction the E.M.F. temperature curve changed in direc-

* " Phil. Mag.," Vol. XLIX., p. 309, March, 1900.
† " Sitzb. der k. Akad. der Wissench.," Vol. LXVI., 1872.
‡ " Sitzb. der k. Akrad. der Wissench.," Vol. LXXI., 1875.
§ " Annalen der Physik," Vol. XLV., 6, pp. 839-860, 1914.

tion at the melting point, and became horizontal up to 300°C., beyond which it was not traced. He observed also a change at the melting point of an alloy of antimony and cadmium when joined with constantan. The results embodied in the present Paper include measurements of E.M.F. against temperature up to 560°C. with junctions of bismuth and a variety of metals, and are thus an extension of previous work.

Experimental.

In order to maintain the circuit after fusion, a salamander crucible, *A* (Fig. 1), was inserted in a sheet of uralite so as to leave the upper rim projecting about 0·5 cm. A groove was cut in the uralite, and a corresponding groove filed in the crucible, so that the molten metal could overflow into the channel in the uralite. This channel was filled with bismuth

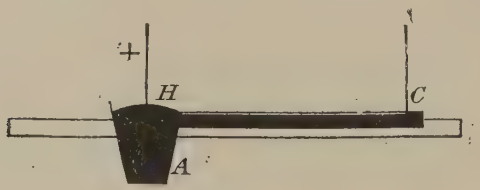


Fig. 1.

to a distance of about 50 cm. from the crucible, where a cold junction, *C*, was formed with the metal under test, which was fused into the bismuth. The hot junction, *H*, was made by dipping the metal directly into the crucible, or, in cases where the metal was attacked by the bismuth, by surrounding the wire by a tight graphite sheath which was immersed in the crucible. Temperatures were measured by means of a carefully calibrated iron-constantan junction, protected by a graphite tip, and immersed in the bismuth side-by-side with the hot junction. Some of the earlier results were checked with a pressure thermometer, which was broken and could not be replaced. The solidification of the bismuth served as a check to the pyrometer in each experiment, and in no case was a greater discrepancy than 2 deg. observed. The temperature of the cold junction was taken from a thermometer placed with its bulb touching the junction, and varied between 18 deg. and 20 deg. on different days, not being noticeably affected by the flow of heat along the bismuth. The crucible was heated by a Méker burner, which proved capable of raising the tempera-

ture to nearly 600°C. E.M.F.s were measured directly on a potentiometer made by the Cambridge Scientific Instrument Company, this instrument being specially suited for thermo-electric work. A Weston cadmium cell was used as standard, and two sets of cooling readings were taken with each junction, which generally showed a good agreement, frequently to within 0·1 mv. In drawing the temperature-E.M.F. curves average values were taken to the nearest $\frac{1}{20}$ mv. Owing to the long time taken in cooling, observations below 100 deg. were not usually made, as such did not bear on the object of the investigation. The results obtained are shown in the following Table :—

Temp. of hot junction.	E.M.F. in millivolts, Bismuth with												
	Copper.	Iron.	Aluminium	Nickel.	Brass.	Silver.	Constantan ?	German Silver.	Nichrom.	Graphite.	Platinum.		
104°C.	5·75	6·40	5·70	4·35	5·60	6·55	4·25	4·85	5·65	6·15	5·50		
126	7·50	8·10	7·15	5·60	7·35	8·30	5·40	6·15	7·35	7·85	7·05		
148	9·00	9·60	8·75	6·65	8·90	10·05	6·50	7·50	8·90	9·50	8·45		
172	10·60	11·50	10·05	7·90	10·40	11·70	7·65	8·75	10·70	11·40	10·00		
192	12·00	13·00	11·75	8·85	11·95	13·50	8·55	9·95	12·10	12·90	11·40		
216	13·60	14·25	12·75	9·70	13·30	15·00	9·45	10·90	13·55	14·30	12·70		
238	14·80	15·30	13·60	10·40	14·55	16·25	10·05	11·70	14·75	15·70	13·70		
260	15·70	16·30	14·65	10·75	15·45	17·25	10·40	12·20	15·80	16·65	14·45		
269 m.pt.	15·75	16·30	14·65	10·75	15·75	17·65	10·45	12·30	15·80	16·65	14·90		
284	15·95	16·40	14·70	10·15	15·70	17·45	9·85	11·95	15·80	16·90	14·70		
305	16·00	16·45	14·70	9·60	15·60	17·35	9·45	11·45	15·80	16·80	14·55		
328	16·10	16·50	14·65	9·00	15·50	17·30	8·90	10·90	15·75	16·70	14·40		
352	16·20	16·50	14·65	8·50	15·35	17·30	8·35	10·25	15·75	16·55	14·25		
372	16·35	16·50	14·70	7·95	15·30	17·25	7·55	9·75	15·75	16·45	14·05		
396	16·40	16·50	14·90	7·55	15·25	17·30	6·80	9·15	15·75	16·40	13·85		
418	16·60	16·40	14·90	7·20	15·25	17·30	6·10	8·40	15·75	16·30	13·70		
440	16·75	16·40	14·95	6·80	15·25	17·25	5·20	7·80	15·85	16·20	13·50		
464	16·85	16·40	15·00	6·30	15·35	17·20	4·45	7·40	15·90	16·05	13·30		
486	16·95	16·50	15·00	5·90	15·40	17·10	3·65	6·80	16·05	15·90	13·15		
508	17·10	16·60	14·65	5·60	15·50	17·15	2·95	6·20	16·20	15·75	12·90		
532	17·20	16·65	14·75	5·30	15·60	17·30	2·55	5·75	16·35	15·65	12·80		
553	17·25	16·60	14·75	4·85	15·70	17·35	1·50	5·10	16·40	15·50	12·65		

Cold junction, 18° to 20°.

Interpretation of Results.

The results obtained show in all cases a marked change in thermo-electric properties at the melting point of bismuth, the nature of the change, however, depending on the second metal. Fig. 2 represents the temperature-E.M.F. curves of copper, silver and nickel, and it will be noticed that at the melting point of the bismuth an abrupt change occurs in each instance. In the case of copper, a small but steady increase in E.M.F. is

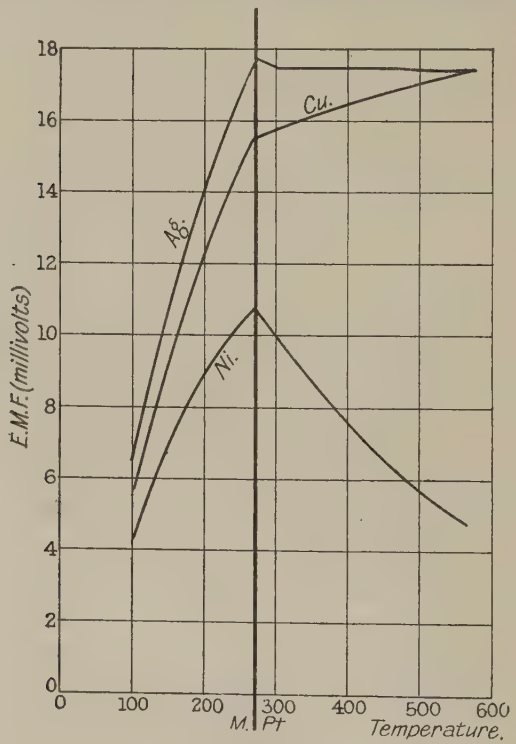


Fig. 2

observed after fusion; with silver the E.M.F. is practically stationary between 300 deg. and 500 deg.; whereas a rapid fall in E.M.F. occurs with nickel. The other metals experimented with give curves resembling one or other of the typical examples shown. Brass shows a slight fall in E.M.F. between 280 deg. and 350 deg., after which a slow, steady rise is observed. Iron, aluminium and nichrom resemble silver in producing a stationary or nearly stationary E.M.F. with the fused bismuth.

German silver and constantan give curves resembling that of nickel; whilst graphite and platinum show a more gradual but continuous fall in E.M.F. after the bismuth has melted. The sample of constantan wire was purchased as such, but did not give so large an E.M.F. either with solid bismuth or iron as is generally attributed to this alloy, and was probably different in composition to the ordinary material.

No attempt was made to construct a thermo-electric diagram from the results—as it would be impossible to obtain correct values of dE/dt at all parts of the curves, many of which show small flexures—without making measurements of a much higher order of accuracy in the region of these flexures. This would involve temperature measurements of a greater degree of refinement than is possible with the methods employed; and it is doubtful whether any conclusions of value could be deduced from such a diagram even after specially accurate results had been obtained. When the temperature-E.M.F. curves are parabolic, and thermo-electric powers may be represented by a straight line, the diagram may be of service; but as this does not apply to the greater part of our results no attempt in this direction has been made. We may point out here that the diagram originally given by Tait, and still reproduced in books is in error, as showing a neutral point in the case of iron and lead between 350 deg. and 400 deg., followed by a diminishing E.M.F. Using the experimental methods described in the present Paper, we find the E.M.F. of a lead-iron junction rises continuously up to 650 deg., and that the neutral point supposed to exist about 40 deg. above the melting point of lead is purely imaginary, having been arrived at by unjustified extrapolation. The usual form of thermo-electric diagram, consisting of a number of straight lines crossing at various points, is of interest mathematically, but is quite unsafe as a guide to the thermo-electric properties of metals over long temperature ranges, and particularly so when extrapolated beyond the fusion points.

The nearly constant E.M.F. observed with silver, aluminium, iron and nichrome over a range of nearly 200 deg. beyond the melting point of bismuth suggests the possibility of a steady thermal source of E.M.F., the value of which would be approximately 17, 15, 16·5 and 16 mv., taking the metals in the order given above. An E.M.F. of this order of magnitude is used in thermo-electric pyrometers in opposition to the hot junction, so as to enable the whole scale to be used for a given range of

temperature—say, 500 deg. to 1,000 deg.—the opposing E.M.F. preventing the movement of the indicator until overcome by that of the hot junction. At present a cell, broken down by resistances is employed to furnish this counter E.M.F., repeated adjustment by reference to a standard cell being necessary as the working cell runs down. A thermal cell, if durable, and sufficiently accurate, would be cheaper and simpler in use than the method now employed, and experiments have been carried out with a view to testing the practicability of a thermal cell for this and similar purposes. It is quite simple to adjust a gas flame so that the temperature of the molten bismuth does not exceed an assigned limit, such as 400 deg., and practical permanence of the temperature of the cold junction can be secured by surrounding it with water. In order to discover whether repeated heating caused any change in the E.M.F., an Al-Bi junction was heated for a total of 70 hours without any alteration being detected; and in no case has prolonged heating been observed to alter the E.M.F. A difficulty, not yet overcome, is the oxidation of the bismuth, which takes place to such an extent as ultimately to break the circuit. Work is still in progress with a view to finding which of the four metals named is the best for practical service, and to secure permanence by preventing oxidation. One drawback to the use of aluminium is that if heated above 370 deg. the E.M.F. rises in value from 14·7 to 15·0 mv. at 460 deg, further heating causing the value to fall to 14·75 at 530 deg.; and hence 370 deg. is the highest permissible temperature. This leaves a range of only 100 deg. over which the E.M.F. is constant to within 0·05 mv., and would necessitate careful regulation of the flame. With silver, the corresponding range is between 320 deg. and 440 deg.; with iron, 300 deg.-400 deg.; and with nichrom 270 deg.-420 deg. The last-named appears to be the most promising, but no final conclusion can be arrived at until prolonged tests have been made. For any temporary purpose, however, an arrangement such as that described in Fig. 1 may be used as a steady source of low E.M.F., using nichrom wire and a flame just sufficiently high to keep the bismuth melted. This will be found useful in measuring low E.M.F., evaluating galvanometer deflections and similar operations.

It is evident, from the results, that molten bismuth cannot be utilised for the measurement of temperatures. Its thermo-electric properties, after fusion, are different from those of tin, lead, zinc and cadmium, all of which show no marked discon-

tinuity as the result of fusion. Preliminary experiments with antimony suggest a similarity to bismuth in this respect, but owing to the higher melting point of the former (632°C.) the apparatus used with bismuth is unsuitable. An electric heating arrangement is under construction with which it is hoped to attain temperatures of 1,000 deg., in order that the properties of various fused metals may be examined over a wider range.

The present investigation has been carried out in the Heat Laboratory of the City and Guilds Technical College, Finsbury, E.C.

ABSTRACT.

One of the authors has for some time been investigating the possibility of using base metal thermocouples at temperatures above the melting point of one of the constituents. For this purpose it was necessary to determine whether any peculiarities in the thermo-electric behaviour of metals occur at fusion. In the case of lead, tin, zinc and cadmium there is no perceptible break in the continuity of the curves obtained. In couples containing bismuth, however, several cases were noted in which the E.M.F. remained constant for a wide range of temperature after the fusion of the bismuth. This occurs with silver, aluminium, iron or nichrom as the other element. Useful applications of this property are discussed. No attempt was made to construct a thermo-electric diagram from the results, as it would be impossible to obtain correct values of dE/dt at all parts of the curves, many of which show small flexures, without making more accurate measurements in the region of such flexures than was practicable.

DISCUSSION.

Mr. A. CAMPBELL, in a communication which was read by the Secretary, remarked that he had made similar experiments (Proc. Roy. Soc., Edin., 1888) on Wood's metal, an alloy of bismuth melting at 73°C. The results of measurements against iron from 8°C. to 150°C., when reduced to a thermo-electric diagram, gave one straight line up to the melting point, and another straight line, of a different slope, above the melting point. He disagreed entirely with the authors' remark son the usual thermo-electric diagram. A diagram of the thermo-electric powers was most valuable, even though the lines may not be straight at the extreme temperatures. If anything is to be deduced from observed results, the first step is to plot the thermo-electric powers against temperature. Why the authors give results of tests against a whole series of metals is not clear. A set of tests against one metal would have been sufficient to fix the bismuth curve on the thermo-electric diagram, and all the other results could then have been deduced from the curves of the other metals already determined by more exact methods.

The PRESIDENT expressed himself puzzled by the results shown in Fig. 2. Up to the melting point of bismuth the different metals gave with it increasing E.M.F.s. At the melting point, however, discontinuities occurred, and it appeared that if one eliminated bismuth by subtracting the ordinates of one curve from another, discontinuities would also occur, at the melting point of bismuth, in the properties of the couples obtained by combining the other metals *inter alia*. This, of course, was not true.

Prof. HOWE pointed out that there was not a marked discontinuity in the difference of the nickel and copper curves when this was plotted. The President's remarks held, however, in the case of silver with either of the others.

Mr. S. W. SMITH pointed out that bismuth was abnormal in that it contracts on melting.

Dr. R. S. WILLOWS mentioned that the metals lead, tin, zinc and cadmium, which had been shown to have no thermo-electric discontinuities at their melting points, happened to be those which, as Mathiessen had found, formed alloys with one another of which the specific resistance could be deduced from the percentage composition. He suggested that the discrepancy mentioned in the case of iron might possibly be due to the occurrence of some allotropic modification, in which case there was really a change in the substance, and it was unfair to extrapolate the thermo-electric diagram beyond the change point.

Mr. DARLING, in reply, said he had no doubt that Mr. Campbell's remarks would hold if one could get out the proper thermo-electric diagram. Owing to the numerous little kinks which occur, very sensitive temperature measurements are required. If really accurate diagrams could be obtained it might then be possible to deduce the properties of any bismuth couple from those of one, as Mr. Campbell suggested. They had tried this in a few cases, however, but did not get good agreement. He did not know whether the peculiarity of bismuth which had been mentioned was related to the phenomena which they had described. Bismuth was a freak metal in many respects. He was unable at the moment to solve the difficulty raised by the President. Their aim had been, primarily, a practical one, and they had not gone as fully into points of that nature as might have been desired.

PUBLICATIONS OF THE PHYSICAL SOCIETY.

THE SCIENTIFIC PAPERS
OF THE LATE
SIR CHARLES WHEATSTONE, F.R.S.
Demy 8vo, cloth. Price 8s.; to Fellows, 4s.

Uniform with the above.

THE SCIENTIFIC PAPERS
OF
JAMES PRESCOTT JOULE, D.C.L., F.R.S.
Vol. I. 4 Plates and Portrait, price 12s.; to Fellows, 6s.
Vol. II. 3 Plates, price 8s.; to Fellows, 4s.

PHYSICAL MEMOIRS.
PART I.—VON HELMHOLTZ, On the Chemical Relations of Electrical Currents. Pp. 110. *Price 4s.; to Fellows, 2s.*
PART II.—HITTORF, On the Conduction of Electricity in Gases; PULUJ, On Radiant Electrode Matter. Pp. 222. *Price 8s.; to Fellows 4s.*
PART III.—VAN DER WAALS, On the Continuity of the Liquid and Gaseous States of Matter. Pp. 164. *Price 8s.; to Fellows, 4s.*

REPORT ON RADIATION AND THE QUANTUM-THEORY
By J. H. JEANS, M.A., F.R.S.
Price 6s.; to Fellows, 3s. Bound in Cloth, 8s. 6d.; to Fellows, 5s. 6d.

PROCEEDINGS.
The "Proceedings" of the Physical Society can be obtained at the following prices:—
Vol. I. (3 parts) bound cloth, 15s.
Vols. II., IV., V., XXIII., XXV., XXVI. & XXVII. (5 parts each), bound cloth, 23s.
Vols. III., VI. to XII. & XXII. (4 parts each), bound cloth, 19s.
Vol. XIII. (13 parts, each containing Abstracts), bound cloth (without Abstracts), 47s.
Vols. XIV. & XV. (12 parts, each containing Abstracts), bound cloth (without Abstracts), 23s.
Vols. XVI. & XIX. (8 parts each), bound cloth, 35s.
Vols. XVII., XVIII. & XXI. (7 parts each), bound cloth, 31s.
Vol. XX. & XXIV. (6 parts), bound cloth, 27s.
Most of the parts can be purchased separately, price 4s. by post 4s. 3d. Fellows can obtain the *Proceedings* (in parts) for their personal use at half the above prices.

ABSTRACTS OF PHYSICAL PAPERS
FROM FOREIGN SOURCES.
VOLS. I. (1895), II. (1896), and III. (1897), 15s. each; to Fellows, 7s. 6d. each.

Strong cloth cases for binding the "Proceedings," price 1s. 6d. each, post free.

BLAKESLEY, T. H. A Table of Hyperbolic Sines and Cosines. *Price 1s. 6d.; to Fellows, 9d.*
LEHFELDT, R. A A List of Chief Memoirs on the Physics of Matter. *Price 2s.; to Fellows, 1s.*

Applications for the above Publications should be sent direct to
"THE ELECTRICIAN" PRINTING & PUBLISHING CO., LTD.,
1, 2 AND 3, SALISBURY COURT, FLEET STREET, LONDON.

CONTENTS.

PAGE

I. The Application of the Kerr Effect to the Determination of the Saturation Values for Magnetism of Ferro-magnetic Metals, Compounds and Alloys. By S. G. Barker, D.I.C., Ph.D., King Edward VII. Research Scholar 1

II. The Influence of the Time Element on the Resistance of a Solid Rectifying Contact. By David Owen, B.A., B.Sc., Birkbeck College and Borough Polytechnic Institute, London 33

III. On Diffusion in Liquids. By Basil W. Clack, M.Sc. (Lond.), Lecturer in Physics at Birkbeck College 49

IV. On the Measurement of the Thomson Effect in Wires. By H. Redmayne Nettleton, M.Sc., Assistant Lecturer in Physics at Birkbeck College 59

V. On the Thermo-electric Properties of Fused Metals. By Charles Robert Darling, A.R.C.S., F.I.C., and Arthur W. Grace 82